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Vol. 3 OCTOBER, 1929 No. 4

CONTENTS

RP. No.	TITLE AND AUTHOR	Page
108.	Compressive strength of clay brick walls. A. H. Stang, D. E. Parsons, and J. W. McBurney	507
109.	Determination of manganese in steel and iron by the persulphate-arsenite method. H. A. Bright and C. P. Larrabee	573
110.	Determination of fluorine and of silica in glasses and enamels containing fluorine. J. I. Hoffman and G. E. F. Lundell	581
111.	The heat of formation of sulphur dioxide. J. R. Eckman and Frederick D. Rossini	597

BUREAU OF STANDARDS JOURNAL OF RESEARCH

CONTENTS OF RECENT NUMBERS

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[Continued on page 3 of cover]

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COMPRESSIVE STRENGTH OF CLAY BRICK WALLS

By A. H. Stang, D. E. Parsons, and J. W. McBurney

ABSTRACT

Compressive tests of 168 walls of common brick, each 6 feet long and about 9 feet high and of 129 wallettes, about 18 inches long and 34 inches high, were made. Four kinds of brick, 3 mortar mixtures, 2 grades of workmanship, different curing conditions, and 10 different types of masonry (3 solid and 7 hollow) were the variables.

Wall strengths were more closely related to the shearing strength of the single brick than to any other strength property of the brick. On the average, the compressive strength of the wallettes was by far a better measure of the strength of the walls than any of the brick strength values. The use of cement mortar gave higher wall strengths than of cement-lime mortar and much higher than if lime mortar was used. For the solid walls the strength varied about as the cube root of the compressive strength of the mortar cylinders, 2-inch diameter and 4-inch length, cured on the walls. Large differences in strength due to differences in workmanship were found. The walls having smoothed-off spread-mortar beds and filled joints were much stronger than walls in which the horizontal mortar beds were furrowed by the mason's trowel. Some of this difference in strength might be ascribed to difference in the filling of the vertical joints. Some of the walls laid in cement mortar were kept damp for seven days after construction. These walls were not stronger than similar walls cured under ordinary conditions in the laboratory.

The solid walls were stronger than the hollow types. With bricks of rectangular cross section the hollow wall strengths varied about as the net areas in compression. When the bricks were not truly rectangular in section, the strength of the hollow walls was found to be less than that expected from the net area. Construction data are given which show the relative saving in materials and time for the hollow types. The results of the wallette tests confirm, in general, the conclusions deduced from the wall tests.

CONTENTS

	Page
I. Introduction	508
II. Scope and purpose of the tests	509
III. Description of specimens and the testing methods	511
1. Bricks	511
(*a*) Description of the bricks	511
(*b*) Test methods	512
(1) Compressive tests	512
(2) Transverse tests	513
(3) Tensile tests	513
(4) Shear tests	513
(5) Absorption tests	513
2. Mortar	514
3. Walls	515
(*a*) Types	515
(*b*) Size	517

III. Description of specimens and the testing methods—Continued.
3. Walls—Continued. Page
(c) Workmanship 518
(1) Series 1 518
(2) Series 2 518
(d) Method of construction 519
(e) Construction data 520
(1) Rate of building 520
(2) Materials used 523
(3) Comparative construction data for different types of walls 523
(4) Thickness of mortar joints 525
(f) Aging conditions 525
(1) Schedule of building 526
(2) The laboratory 526
(3) Damp-cured walls 526
(g) Age 526
(h) Testing machine 526
(i) Method of testing 528
4. Wallettes 528
IV. Results of the tests with discussion 528
1. Brick 528
2. Mortar 531
3. Walls 532
(a) Basis of computations 532
(b) Deformation of the walls 532
(1) Stress-strain curves 532
(2) Secant modulus of elasticity 534
(3) Permanent set 539
(c) Behavior of the walls under load 539
(d) Compressive strength 540
(e) The comparative strengths of solid and of hollow walls of brick 540
(f) The effect of mortar on the strength of walls otherwise similar 545
(g) The effect of damp curing on the compressive strength of brick walls 548
(h) The effect of the quality of workmanship on wall strength 551
(i) The relation of stress at first crack to the maximum stress 555
4. Wallettes 556
5. Relations between the strengths of the walls and the strengths of the bricks and wallettes 563
V. Conclusions 568
VI. Appendix 569
1. Reports on workmanship 569
(a) Comments by J. W. Ginder 570
(b) Comments by A. L. Harris 571

I. INTRODUCTION

At a conference held at the Bureau of Standards in 1921, attended by representatives of the clay, sand-lime, and cement brick industries,

it was agreed that the bureau should make tests which would afford a comparison of the strength of masonry built of these three kinds of brick.

Tests of walls built of sand-lime brick have been made and the results reported in Technologic Paper No. 276. The present paper reports and discusses the results of the tests on clay brick masonry. In this report walls numbered 1 to 17 are of such construction as to permit comparison with those built of sand-lime brick, but it should be noted that the sand-lime brick used were of slightly higher compressive strength than those used in the construction of walls 1 to 17, inclusive. The effect of brick strength on wall strength is discussed herein. The tests on masonry of cement brick have not yet (1929) been made.

The scope of this investigation has been extended much beyond the original plan, for it seemed desirable to discover, if possible, some of the factors which influence or measure masonry strength. It is believed that much pertinent information, not heretofore known and analyzed, has been disclosed and that this information may be useful to engineers and architects and to the construction industry generally.

The present construction trend is toward a more economical use of material, but it is obvious that a handicap is imposed upon any structural material if the "factor of uncertainty" is large. Brick masonry has been under such a handicap in the past, for few tests have been made on specimens which fairly represent brick walls as used in construction. Tests of brick masonry made heretofore have been principally of piers and small wall sections, and results have not been conclusive for two reasons: (1) Uncertainty has existed as to the relationship between the stress producing failure in these small specimens and that in brick walls as used in structures; (2) previous reports have given but little data on the effect of the various physical properties of individual bricks, and especially on the effect of workmanship on wall strength.

Realizing these conditions, the Bureau of Standards, cooperating with the Common Brick Manufacturers' Association of America, undertook the investigation reported herein.

II. SCOPE AND PURPOSE OF THE TESTS

This investigation deals with the compressive tests under central loading of 168 brick walls each 6 feet long and about 9 feet high and of 129 wallettes or small walls each about 18 inches long and 34 inches high. A view of several of the walls in the laboratory is shown in Figure 1. Four kinds of common brick, three mortar mixtures, and ten types of wall construction were included. Table 1 gives the wall numbers for the different variables.

TABLE 1.—*Wall specimens*

Type of wall	Mortar	Wall numbers and kind of brick						
		Series 1			Series 2			
		Chicago	Mississippi	New England	Chicago	Detroit	Mississippi	New England
8-inch solid	Lime	1, 2, 3						
	Cement-lime	7, 8, 9				19, 20, 21	34, 35, 36	94, 95, 96.
	Cement	13, 14, 15	155,[1] 159[1]	154[1]	160,[1] 161,[1] 162,[1] 163,[1] 164,[1] 165.[1]	22, 23, 24	37, 38, 39	97, 98, 99.
	Cement-wetted					33		
12-inch solid	Lime	4, 5, 6						
	Cement-lime	10, 11, 12				25, 26, 27	40, 41, 42	100, 101, 102.
	Cement	16, 17			166,[1] 167,[1] 168[1]	28, 29, 30	43, 44, 45	103, 104, 105.
	Cement-wetted					31, 32	46, 47	106, 107.
	Cement-shoved				18		48	108.
8-inch all-rolok	Cement-lime						49, 50, 51	109, 110, 111.[1]
	Cement		156[1]				52, 53, 54	112, 113, 114.
12-inch all-rolok	Cement-lime						55, 56, 57	115, 116, 117.[1]
	Cement						58, 59, 60	118, 119, 120.[1]
8-inch all-rolok in Flemish bond	Cement-lime						61, 62, 63	121, 122, 123.[1]
	Cement		157[1]				64, 65, 66	124, 125, 126.[1]
12-inch all-rolok in Flemish bond	Cement-lime						67, 68, 69	127, 128, 129.[1]
	Cement						70, 71, 72	130, 131, 132.[1]
8-inch rolok-bak	Cement-lime						73, 74, 75	133, 134, 135.[1]
	Cement		158[1]				76, 77, 78	136, 137, 138.[1]
12-inch rolok-bak (heavy duty)	Cement-lime						79, 80, 81	139, 140, 141.[1]
	Cement						82, 83, 84	142, 143, 144.[1]
	Cement-wetted						85, 86	145, 146.
12-inch rolok-bak (standard)	Cement						87	147.[1]
4-inch Economy	Cement-lime						88,[1] 89,[1] 90[1]	148,[1] 149,[1] 150.[1]
	Cement						91,[1] 92,[1] 93[1]	151,[1] 152,[1] 153.[1]

[1] No wallette built with these walls.

The walls are divided into two series based on the grade of workmanship. A contract for building the walls of series 1 was let on a lump-sum basis to a brick mason who specialized in small contracts and who laid the bricks for all walls in the series. The walls of series 2 were built under rather careful supervision by a mason who was hired by the day.

It is hoped that the data obtained from these tests will be valuable for the purposes listed below.

1. To determine the relation between the several physical properties of the bricks and the strength of walls built therefrom.
2. To obtain the comparative strengths of different types of solid and of hollow walls of brick.
3. To determine the effect of damp curing on the compressive strength of brick walls.
4. To determine the relation between the strength of the mortar and the strength of the wall.
5. To determine the effect of the quality of workmanship on wall strength.
6. To compare the compressive strengths of masonry specimens of different sizes.

III. DESCRIPTION OF SPECIMENS AND THE TESTING METHODS

1. BRICKS

(a) DESCRIPTION OF THE BRICKS

Four kinds of common bricks were used in building the specimens for this investigation. As the principal differences between these bricks are in the method of manufacture, a short description of the methods of forming is here introduced.

Bricks are usually formed by the soft-mud, dry-press, or stiff-mud processes. In the soft-mud process the clay is reduced with water to a semiliquid consistency and formed in molds with slight pressure. Usually the molds are first dampened and then sanded before use, thus giving the bricks a finish which is commonly termed "sand struck." The dry-press process resembles the soft-mud process except that much less water is used, resulting in a stiffer mixture, and the bricks are formed in molds under considerable pressure. In the stiff-mud process the clay mixture is extruded from an orifice or die in a continuous column which is cut to form the individual bricks. If the cross section of the column is approximately 8 by 3¾ inches and the cuts are 2¼ inches apart, there results what are known as "side-cut" bricks. If the column has a cross section approximately 2¼ by 3¾ inches and the cuts are 8 inches apart, the term "end-cut" is applied to the bricks. Sometimes double or triple dies are used on

one machine, but the columns are cut in the same manner as when but one is used.

For convenience these bricks are designated by the name of the region in which they were made and are described as follows:

Chicago.—These bricks were made from surface clay and formed by the end-cut, double-column, stiff-mud process. They are rather irregular in shape and contain lime nodules.

Detroit.—These bricks were formed by the soft-mud process from surface clay. Like many soft-mud bricks, they were formed with a frog or depression in one face approximately 0.4 inch deep. These Detroit bricks resemble the soft-mud bricks from the Cleveland (Ohio) region.

Mississippi.—These were surface-clay bricks formed by the dry-press process. Regularity of size and shape was the outstanding characteristic of these specimens.

New England.—These bricks were formed by the soft-mud process from surface clay and were "sand struck." The specimens possessed a shallow frog or depression, were very hard burned, and rather irregular in size and shape.

The average sizes and weights of these bricks, from measurements of 50 specimens of each kind, are given in Table 2.

TABLE 2.—*Average size and weight of the bricks*

Kind of brick	Chicago	Detroit	Mississippi	New England
Length, inches	7.84	8.16	8.20	7.88
Width, do	3.60	3.60	3.80	3.34
Thickness, do	2.21	2.46	2.34	2.24
Dry weight per brick, pounds	3.94	4.16	4.20	4.56
Weight, pounds per cubic foot	109	99	99	126

(b) TEST METHODS

The usual tests as outlined by the American Society for Testing Materials,[1] of compressive strength, modulus of rupture, and water absorption, were made on about 50 bricks of each kind. In order to obtain a more complete knowledge of the properties of the brick, still other tests were carried out as outlined below.

(1) COMPRESSIVE TESTS.—The compressive tests of half bricks on edge are the only tests described in the specifications for building brick of the American Society for Testing Materials. It was decided, however, to include also compressive tests of whole bricks edgewise and flatwise. Besides the half bricks tested flatwise and edgewise in a dry condition, an equal number of half bricks were tested when wet. For these tests they were prepared as for the dry tests, immersed

[1] A. S. T. M. Standards, p. 665; 1924.

FIGURE 1.—*Brick walls stored in the laboratory*

Note the mortar specimens on the walls.

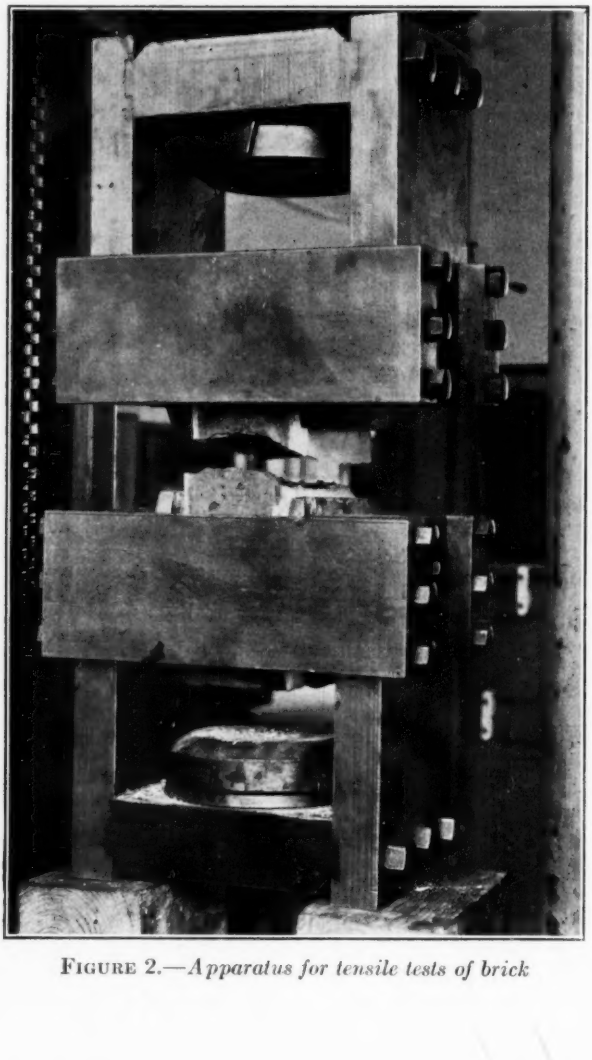

FIGURE 2.—*Apparatus for tensile tests of brick*

in water at room temperature for 48 hours, taken out, and tested within 10 minutes.

The compressive strength was obtained by dividing the maximum load by the sectional area.

(2) TRANSVERSE TESTS.—The bricks for the transverse test were tested on a 7-inch span with a central load and with apparatus recommended by the American Society for Testing Materials. Since in some of the walls the bricks are laid on edge or rowlock, transverse tests were made on brick edgewise as well as flatwise. The modulus of rupture in pounds per square inch was computed from the formula

$$R=\frac{3}{2}\frac{wl}{bd^2}$$

in which

l is the distance between supports, 7 inches,

b is the width of the brick perpendicular to the line of load application, in inches,

d is the depth of the brick parallel with the line of load application, in inches, and

w is the maximum center load in pounds.

(3) TENSILE TESTS.—Tensile tests of the whole brick were made in the apparatus [2] shown in Figure 2. The bricks for these tests were dried and shellacked. The sides of the bricks were than bedded in plaster of Paris to give smooth and parallel surfaces as shown in this figure. The spherical bearings of the apparatus assisted in producing a uniform loading over the cross section of the specimen, and nearly all of the specimens broke in the free length between the ends of the gripping wedges.

The tensile strength was obtained by dividing the maximum load by the product of the width and depth of the brick.

(4) SHEAR TESTS.—Punching shear tests were made with the apparatus designed by H. H. Dutton and described and pictured in Kessler and Sligh's paper on "Physical Properties of the Principal Commercial Limestones Used for Building Construction in the United States." [3] All tests except those on the New England brick were made on halves from the tensile test. Due to the strength of the New England brick, it was found necessary to use thinner test specimens, and consequently the tests were made with slabs 1 inch in thickness sawed from whole bricks.

(5) ABSORPTION TESTS.—Water-absorption tests were made by the 5-hour boiling test and by a 48-hour immersion test. For the former, dry bricks were submerged in water at room temperature, the water

[2] For a more complete description of this apparatus, see J. Am. Ceram. Soc., 11, No. 2, pp. 114-117; February, 1928.

[3] D. W. Kessler and W. H. Sligh, B. S. Tech. Paper No. 349, p. 508.

heated to boiling within 1 hour, boiled continuously for 5 hours, and allowed to cool to room temperature. In the 48-hour immersion test they were immersed in water at room temperature for that period of time. The percentage of absorption was calculated on the dry weight according to the relation

$$\text{Percentage of absorption} = 100\frac{(B-A)}{A}$$

where A is weight of the dry brick and B is the weight of the saturated brick.

2. MORTAR

The mortar mixes represent certain commonly used volume proportions. Measurements by volume, however, would have resulted in wider variations in the mortar compositions than seemed desirable so that equivalent proportions by weight were used, assuming that 1 cubic foot of lime weighs 40 pounds and 1 cubic foot of cement weights 94 pounds. The weight of the dry materials in a cubic foot, loose measure, of the damp sand used on this work was determined by preliminary tests to be about 73 pounds. Since the weight of a cubic foot of damp sand, loose measure, varies with the moisture content, the moisture in a sample of sand was determined each day during the construction of the walls and the weight necessary to make the desired amount of dry sand was computed. This value was used in proportioning the mortar for the day. Water was added to give the consistency desired by the mason and the amount of water recorded. All the mortar used was proportioned by these equivalent weights.

The mortar for walls 1 to 18 and 160 to 162, built of Chicago brick, was mixed in the same proportions as had been used for the sand-lime brick walls, already referred to. These mixtures were as follows:

Lime mortar	By volume, 1¼ parts of hydrated lime to 3 parts of damp sand; weight equivalents, 50 pounds of lime to 220 pounds of dry sand.
Cement-lime mortar	By volume, 1 part of Portland cement, 1¼ parts of hydrated lime, to 6 parts of damp sand; weight equivalents, 94 pounds of cement, 50 pounds of lime, to 440 pounds of dry sand.
Cement mortar	By volume, 1 part of Portland cement to 3 parts of damp sand; weight equivalents, 94 pounds of cement to 220 pounds of dry sand.

The mortar mixtures used in the other walls were cement lime and cement mortars. They differed slightly from the above mixes so as to be in conformity with the mortars recommended for solid walls by the Building Code Committee of the Department of Commerce.[4]

[4] Report of Building Code Committee, Elimination of Waste Series, Recommended Minimum Requirements for Masonry Wall Construction, Department of Commerce, Washington, D. C.

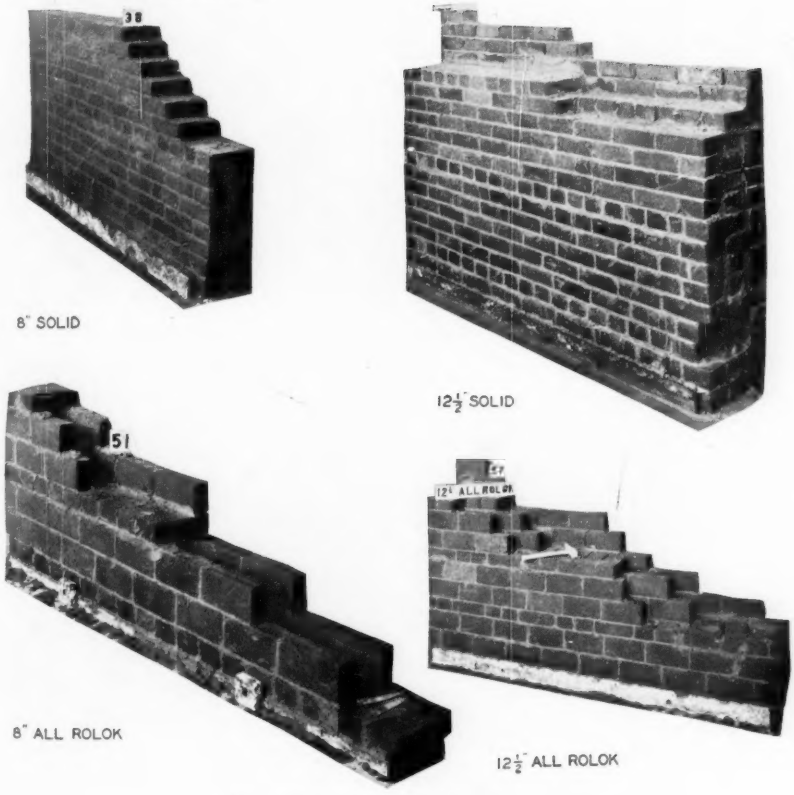

FIGURE 3.—*Types of brick walls*

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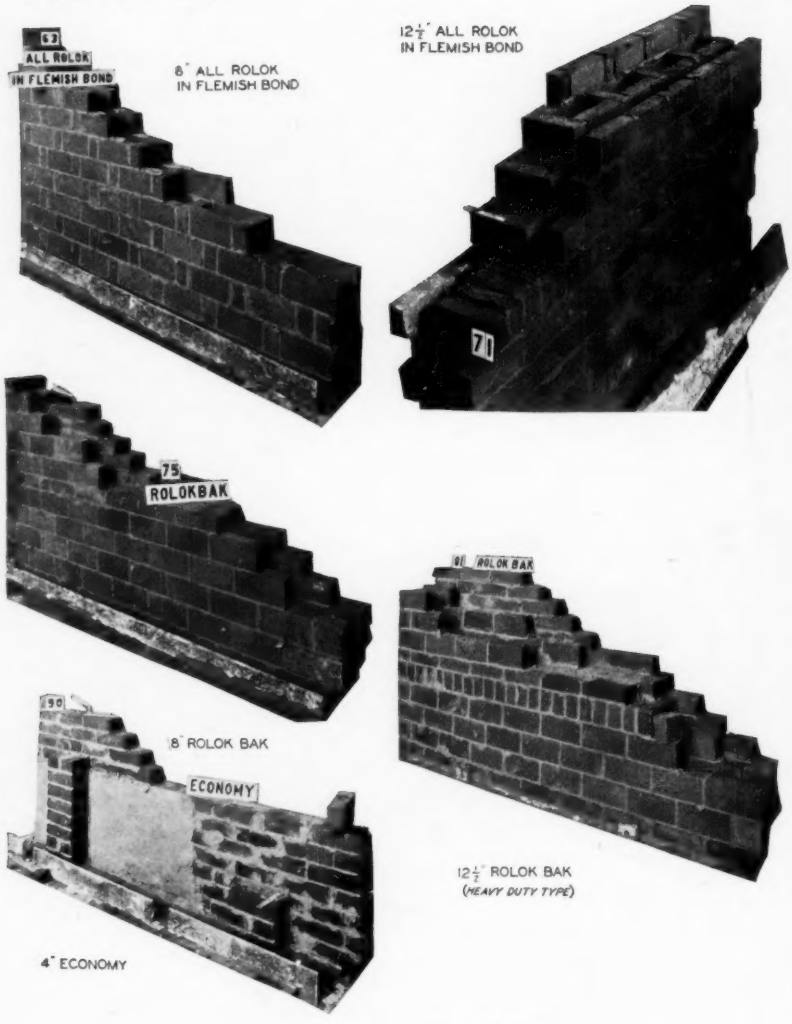

FIGURE 4.—*Types of brick walls*

The mixtures for walls 19 to 159 and 163 to 168 were as follows:

Cement-lime mortar----- By volume, 1 part of Portland cement, 1 part of hydrated lime, to 6 parts of damp sand; weight equivalents, 94 pounds of cement, 40 pounds of lime, to 440 pounds of dry sand.

Cement mortar--------- By volume, 1 part of Portland cement to 3 parts of damp sand (hydrated lime equal to 10 per cent of the volume of the cement was added); weight equivalents, 94 pounds of cement, 4 pounds of lime, to 220 pounds of dry sand.

It is not believed that these mortars differed to an appreciable extent in their effect on brick-wall strength from the corresponding mortars used in the walls of Chicago brick, but a comparison of the cement mortars may be obtained from the results of tests of the two groups, 160 to 162 and 163 to 165.

The Portland cement and the hydrated lime were purchased on the open market and conformed to the requirements of the United States Government purchase specifications, Federal Specifications Board specification Nos. 1a and 249, respectively. The sand was Potomac River sand. All the lime and sand were on hand before any walls were built. The cement was obtained as needed from Government-inspected bins.

Six cylinders (2 inches diameter, 4 inches long) for compressive tests were made from the mortar of each wall, except that for each wall built with lime mortar only three cylinders were made. After they had been taken from the molds, three cylinders were placed on the wall they represented, as shown in Figure 1, and allowed to age in this position. These cylinders will be described as "dry." The other cylinders were placed in water and will be termed "wet." The three cylinders made for each of the lime mortar walls were aged dry because lime mortars disintegrate when placed in water. The cylinders were tested on the same day as the corresponding wall.

3. WALLS

(a) TYPES

Ten different types of brick masonry were included in this investigation. They consisted of three types of solid brickwork, and seven types of hollow walls as follows:

A, 8-inch solid.
B, 12-inch solid.
C, 8-inch all-rolok.
D, 12-inch all-rolok.
E, 8-inch all-rolok in Flemish bond.
F, 12-inch all-rolok in Flemish bond.
G, 8-inch rolok-bak.
H, 12-inch rolok-bak, heavy duty.
I, 12-inch rolok-bak, standard.
J, 4-inch economy walls.

Partially completed walls of each of these types, except that of the 12-inch rolok-bak, standard type, are shown in Figures 3 and 4. Sectional views of the 10 types of construction are shown in Figure 5.

The 8-inch and the 12-inch solid walls were laid in common American bond, having headers each sixth course. The bricks in these walls were laid flat. These types are shown in Figure 3.

The solid walls built with Chicago brick (walls 1 to 18) began and ended with a header course. None of the other solid walls had header courses at the top or bottom.

The hollow walls had header courses at the top and bottom. In the all-rolok walls the stretchers are laid on edge. Every third

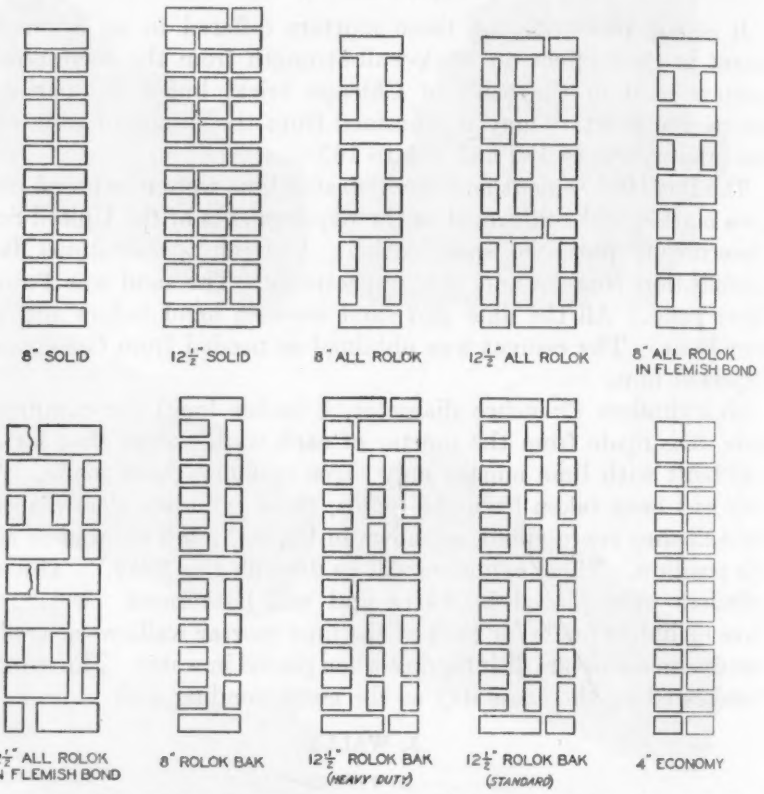

FIGURE 5.—*Sectional views of the types of brick-wall construction tested*

course is a header course with the brick flat. Figure 3 shows that in the 8-inch all-rolok wall the headers are side by side and, of course, extend completely through the wall. The back of a 12-inch wall of this type is also shown in Figure 3. The center withe of brick on edge is not centered in this wall, but is lined up with the outside headers as shown in Figure 5. The header courses are of "basket weave," in which two header bricks joining the face withe with the central withe alternate with two header bricks joining the back withe with the central withe, the spaces opposite each pair of headers being occupied by a single stretcher.

The all-rolok in Flemish bond walls are shown in Figure 4. In these walls all the bricks are on edge laid in Flemish bond for the outside 8-inch width. For the 12-inch wall a withe of stretchers is added, three courses high. The appearance of the front of the wall in the next course is still of the Flemish bond, but the headers of this course are bats and the backing is a continuous course of rowlock headers.

The exterior 4-inch thickness of the rolok-bak walls, shown in Figure 4, is laid with the brick flat and the backing is laid of brick on edge. On the exterior, therefore, the brickwork has the usual appearance of ordinary brickwork having headers each seventh course. Four courses of brick on edge bring the backing courses to the same height as that of the six flat courses of the face. The 12-inch rolok-bak wall, shown in Figure 4, is the heavy-duty type recommended by the Common Brick Manufacturers' Association for heavy load-bearing construction. In this type the fourth backing course consists of rolok-headers. Two 12-inch rolok-bak walls, standard type, were included in this investigation. The standard type differs from the heavy-duty type by having the four backing courses all stretchers, the flat header course being of "basket weave." This difference is shown in Figure 5.

The economy wall shown in Figure 4 is essentially a 4-inch wall with pilasters 8 inches wide and 4 inches thick built into the wall at intervals of about 5½ stretcher lengths. The pilasters were tied to the 4-inch withe with headers each sixth course. All bricks were laid flat. The "economy" walls of this investigation were plastered on the back between the pilasters with the same kind of mortar as that in which they were laid, since this method of construction is recommended for weatherproofing the single withe.

A more extended description of the hollow walls is given in the literature of the Common Brick Manufacturers' Association.[5]

(b) SIZE

The walls were 6 feet long. When necessary, the end bricks were chipped so as to project only slightly beyond the end of the wall, as shown in Figure 1. The height of the walls was about 9 feet.

The thickness of each wall was measured at three different heights on each end and was considered as the average of these six measurements. The length of each wall was considered to be 72 inches, since this was their minimum length and equaled the lengths of the base channels and the platen of the testing machine.

[5] Hollow Walls of Brick and How to Build Them, Common Brick Manufacturers' Association of America, Cleveland, Ohio.

(c) WORKMANSHIP

The walls of this investigation have been divided into two series, each of which was built by a different mason and with a different grade of workmanship. There is at present no scale by which the workmanship can be measured, and, consequently, differences in the quality of the work are difficult to evaluate. The following description may aid in judging the grades of workmanship.

(1) SERIES 1.—Walls 1 to 17 of series 1 were built so as to have the quality of the workmanship directly comparable to that obtained with the sand-lime brick walls which had already been tested at the Bureau of Standards.[6] Bids were obtained from a number of reputable local masons, and the work of building the walls was awarded the lowest bidder, who happened to be the same mason who had built the sand-lime brick walls. This mason received neither instruction nor supervision. Only on wall 159 of series 1 were instructions given and supervision exercised. Characteristics of the work were that there was practically no mortar in the longitudinal vertical joints, the horizontal mortar beds were deeply furrowed, and the brick were laid at a high rate. Figure 6 is an end view of several walls of series 1.

Figure 7 shows a horizontal mortar bed of one of these walls after the test of the wall. The furrows made by the trowel point are plainly visible, and the uneven bedding caused by them must have weakened the wall. Figure 8 shows an end view of a similar wall built with cement-lime mortar. The trowel marks may be plainly seen. In this connection, it should be pointed out that the mason thought that he eliminated the furrows by pressing down and tapping the brick.

Walls 154 to 158 were built by the same mason and with the same grade of workmanship. The hollow brick walls included among these were the first of those types that this mason had built. Wall 159 was also built by the same person. For this wall he was instructed to fill the vertical mortar joints between the withes and not to furrow the horizontal mortar beds with the point of the trowel.

(2) SERIES 2.—The walls of series 2 were built by the other mason, who was employed by the day without regard to output. His work was characterized by complete filling of all vertical joints and smoothing of beds. The filling of vertical joints was accomplished not by the use of "shoved" work but by heavy "buttering" and "slushing" or "dashing" after completion of the course. His original instructions were to use his best workmanship without "shoving" the brick. Near the end of the program he was instructed to use shoved work on the two 12-inch solid walls 48 and 108. It may be of interest to note that he did not require instructions in filling vertical joints, but he

[6] Whittemore and Stang, Compressive Strength of Sand-Lime Brick Walls, B. S. Tech. Paper No. 276

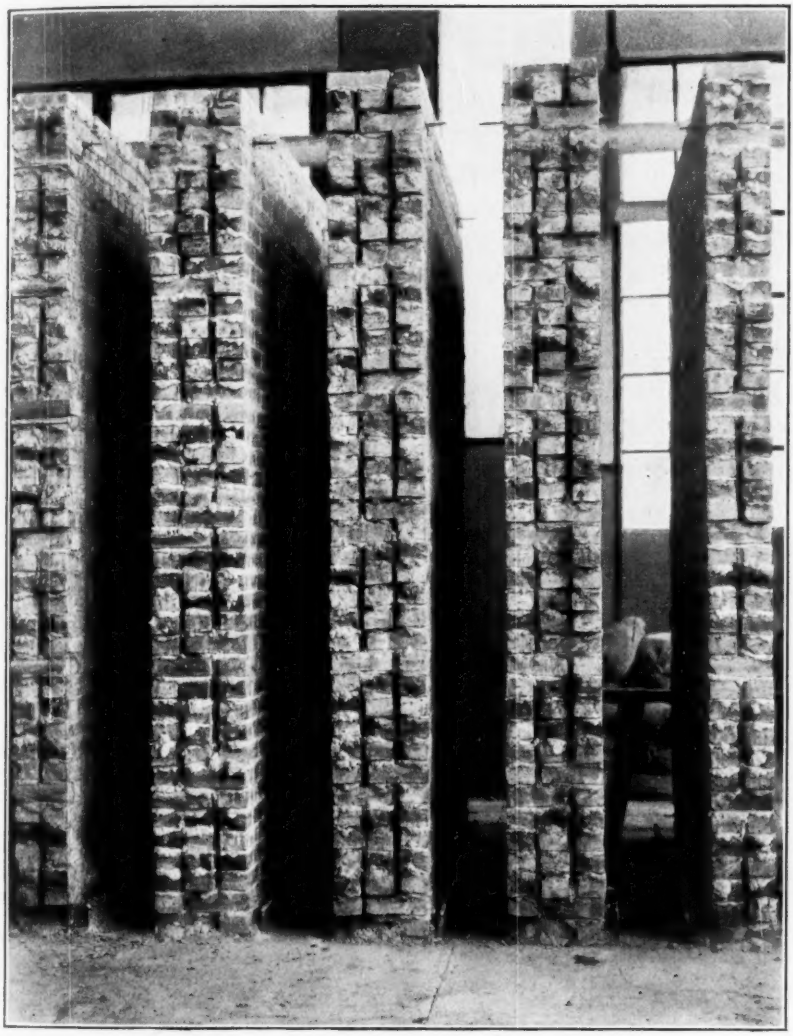

FIGURE 6.—*End view of several walls of series 1*

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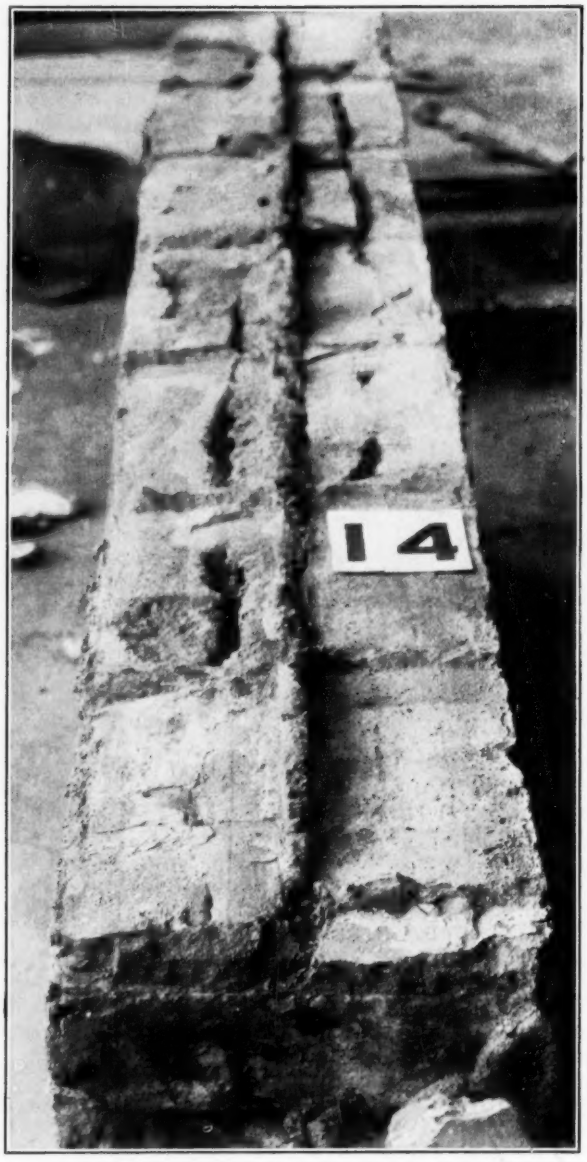

FIGURE 7.—*The mortar bed in a wall of series 1*

Wall 14, an 8-inch solid wall built of Chicago brick, laid in cement mortar.

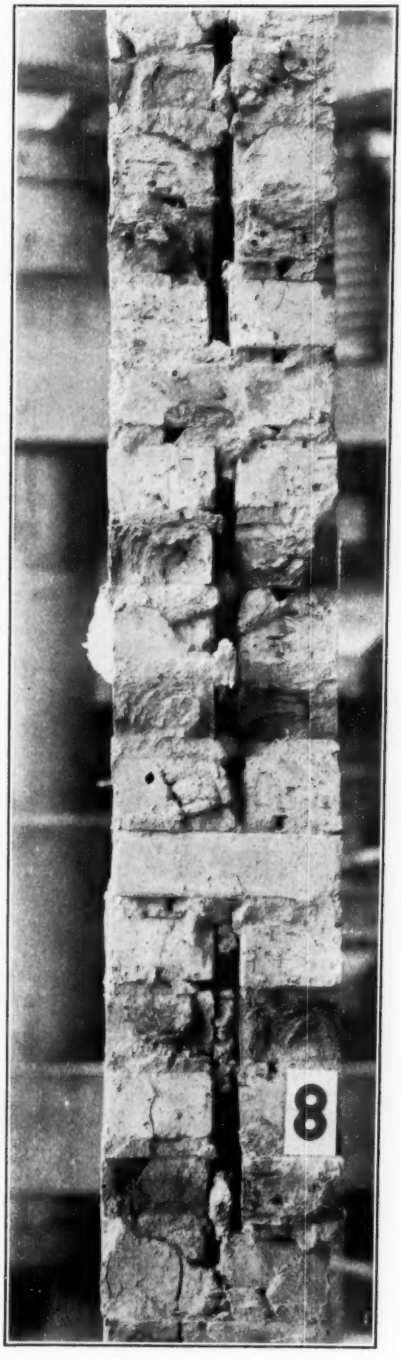

FIGURE 8.—*End view of a wall of series 1 after test*

Wall 8, an 8-inch solid wall built of Chicago brick, laid in cement-lime mortar.

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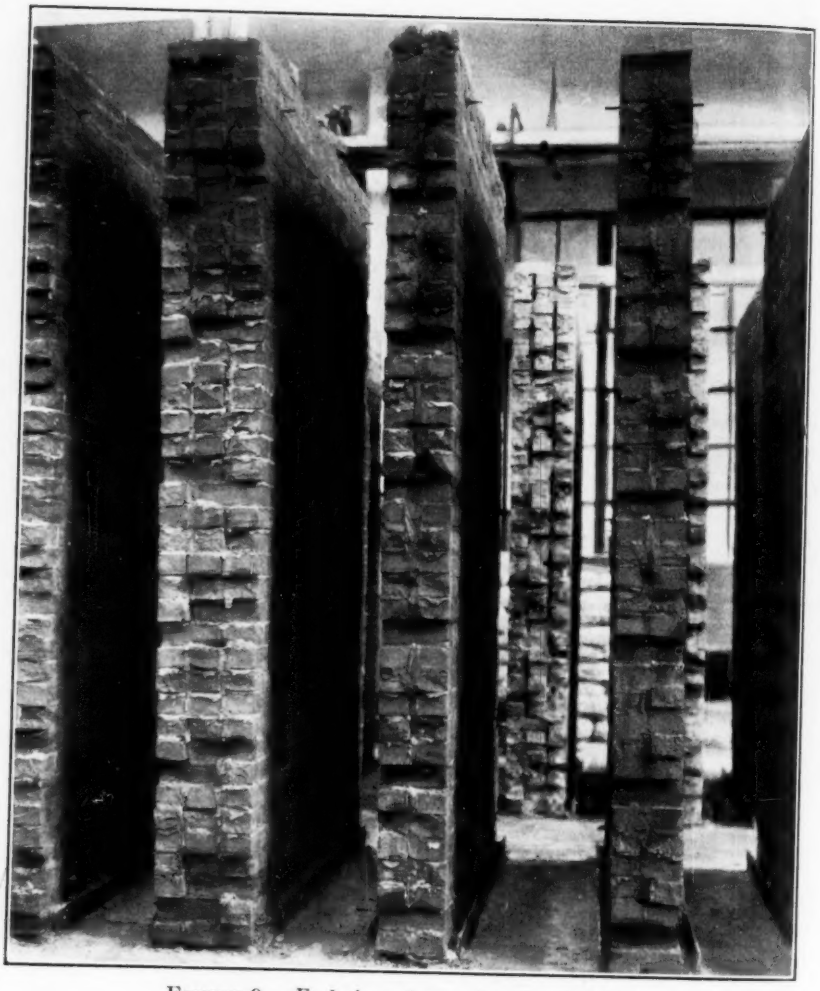

FIGURE 9.—*End view of several walls of series 2*

FIGURE 10.—*The mortar bed in a wall of series 2*

Wall 101, a 12-inch solid wall built of New England brick, laid in cement-lime mortar.

FIGURE 11.—*Characteristics of the horizontal mortar bed (the furrowing) in the walls of series 1*

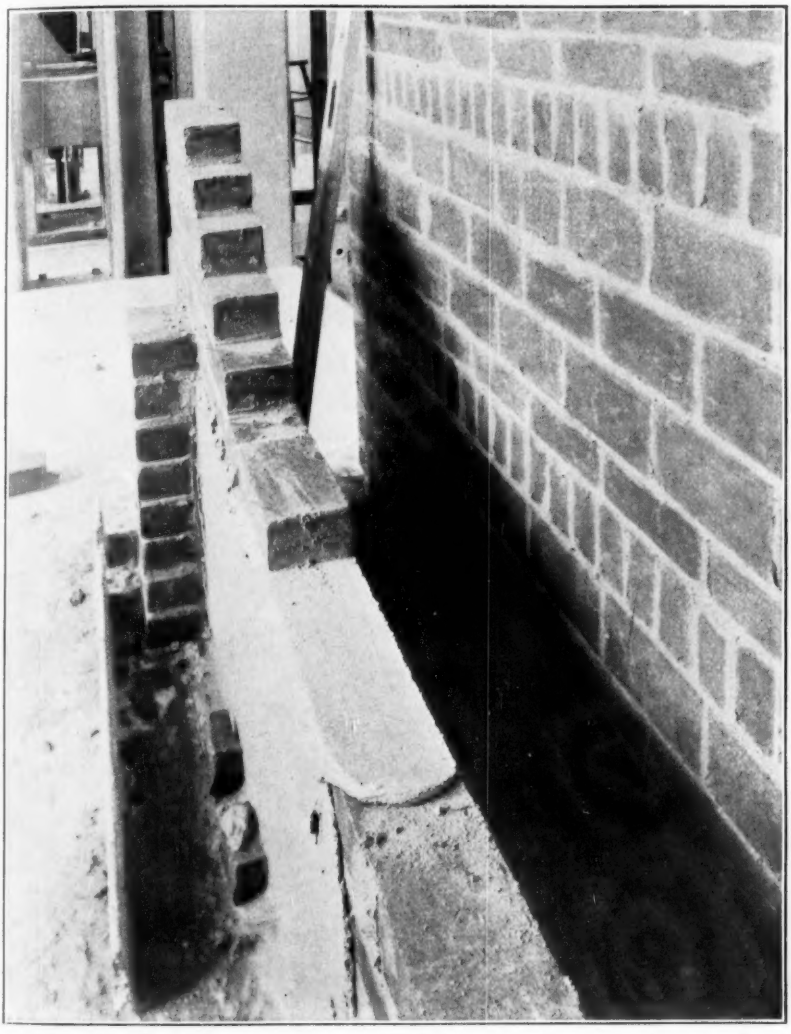

FIGURE 12.—*Carefully leveled horizontal mortar beds in the walls of series 2*

FIGURE 13.—*A portion of wall 18 after test*

Note that the mortar joints are completely filled.

had to be cautioned not to furrow the horizontal beds. However, he later reported that laying smooth spread beds was as easy as laying furrowed ones. He worked at all times very carefully and slowly; in fact, his work would be characterized as "fussy" compared with that of the mason who built the walls of series 1. No difference was noted between the general plumbness of the two men's work.

Figure 9 shows an end view of several walls and Figure 10 a typical mortar bed for the walls for series 2. Figures 11 and 12 are views showing a furrowed bed and a carefully leveled horizontal bed.

It was originally planned to have 18 walls of Chicago brick built in series 1, but sufficient bricks were not available to build the last wall (wall 18). Enough bricks were, however, salvaged from the specimens after the tests of the first 17 walls for another wall. Wall 18 was, therefore, built afterwards by the mason of series 2. He used great care in its construction, and it is doubtful whether better construction could have been obtained. Figure 13 shows a portion of this wall after test and gives an idea of how well all joints were filled.

Two 12-inch solid brick walls of this series laid in cement mortar (walls 48 and 108) were built with "shoved" workmanship. Wall 48 was built of Mississippi brick and wall 108 of New England brick. The object of building these walls was to compare the strength of the shoved work with that of equally careful work not shoved.

The difference in the rate of laying brick by the two masons is believed to be due more to the characteristics of the men than to the methods employed. The reason for this belief is that the mason who built the walls of series 1 worked as fast on the supervised wall (No. 159) as he did on the others.

(d) METHOD OF CONSTRUCTION

The Chicago brick used for walls 1 to 18 were stored in the laboratory and were consequently rather dry. The bricks were placed in a wheelbarrow and a pail of water poured over them. On the average, the brick of these walls were drier when laid than those in the other walls.

The other bricks were piled in the open without arranging them in regular order. Twenty-four hours before they were laid in the wall they were thoroughly sprinkled until the water flowed continuously from every portion of the pile. They were again sprinkled in the same manner just before laying.

Each wall was built on a steel channel, as shown in Figure 6, so it could be moved into the testing machine. Starting on the level channel, the wall was kept plumb and the courses level as the work progressed.

(c) CONSTRUCTION DATA

The average construction data for the walls are given in Table 3. The walls were constructed under careful supervision as to the mixture of the mortar materials and records were kept of the time and materials required. Since these records give construction data which may be used in making estimates for comparing the cost of the several types of walls, it is thought that they are of value to contractors and architects.

(1) RATE OF BUILDING.—The time required to build each wall was recorded, beginning when the base plate was level and ending when the last brick was laid. The time, about 10 minutes, required to erect the scaffold, was included. Table 3 gives the rate of building in square feet of wall surface per hour per mason and also the rate of laying brick per hour. This table shows that the walls of series 1, which were built under contract, were built at a much faster rate than those of series 2, built by day labor under careful supervision.

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TABLE 3.—*Average construction data of brick walls*

A. WALLS OF SERIES 1

Type of wall	Mortar	Kind of brick	Wall Nos.	Average thickness of mortar joints	Rate of building wall	Number of brick laid per hour	Brick per square foot of wall surface	Mortar materials used (pounds per square foot of wall surface)			
								Cement	Lime	Sand (dry)	Water
				Inch	*Sq.ft.hr.*						
8-inch solid	Lime	Chicago	1, 2, 3	0.55	14.4	183	12.7	-------	3.2	14.3	4.8
	Cement-lime	do	7, 8, 9	.55	15.4	195	12.6	3.0	1.6	14.4	4.4
	Cement	do	13, 14, 15	.56	14.1	175	12.4	6.0	-------	13.9	4.1
		Mississippi	155	.73	17.4	195	11.2	5.0	.2	11.8	5.8
		do	159	.62	19.5	264	13.5	7.2	.3	16.9	6.1
		New England	154	.46	15.0	189	12.6	6.1	.3	14.2	4.9
12-inch solid	Lime	Chicago	4, 5, 6	.55	11.9	226	19.0	-------	5.0	22.6	8.3
	Cement-lime	do	10, 11, 12	.56	11.2	212	18.9	4.9	2.6	23.5	7.1
	Cement	do	16, 17	.56	11.6	221	18.9	8.6	-------	20.6	6.2
8-inch all-rolok	do	Mississippi	156	.66	19.2	168	8.7	3.2	.1	7.4	2.9
8-inch all-rolok in Flemish bond	do	do	157	.65	17.5	155	8.9	5.2	.2	12.2	-------
8-inch rolok bak	do	do	158	.62	20.5	206	10.0	3.7	.2	8.8	-------

B. WALLS OF SERIES 2

8-inch solid	Cement-lime	Detroit	19, 20, 21	0.41	8.0	94	11.7	3.8	1.6	18.0	5.5
		Mississippi	34, 35, 36	.47	7.7	95	12.3	3.3	1.4	15.3	4.3
		New England	94, 95, 96	.30	7.7	104	13.5	2.7	1.1	12.9	4.4
	Cement	Chicago	160, 161, 162	.57	9.1	118	12.9	7.9	-------	18.4	6.2
		do	163, 164, 165	.62	8.8	115	13.1	7.8	.3	18.4	6.1
		Detroit	22, 23, 24, 33	.40	8.2	96	11.7	7.4	.3	17.3	5.6
		Mississippi	37, 38, 39	.45	7.2	89	12.4	5.7	.3	13.4	4.3
		New England	97, 98, 99	.28	7.2	98	13.7	5.3	.2	12.4	4.2
12-inch solid	Cement-lime	Detroit	25, 26, 27	.40	5.8	101	17.4	6.1	2.4	27.3	8.2
		Mississippi	40, 41, 42	.45	6.1	113	18.6	4.6	2.0	21.7	7.4
		New England	100, 101, 102	.26	5.6	117	21.3	5.1	2.2	24.0	6.1
	Cement	Chicago	18	.31	6.4	127	20.0	10.0	-------	23.3	7.5
		do	166, 167, 168	.51	6.2	123	19.9	11.0	.4	25.7	8.8
		Detroit	28, 29, 30, 31, 32	.39	6.6	116	17.7	10.4	.5	24.3	7.7
		Mississippi	43, 44, 45, 46, 47, 48	.42	5.2	97	18.7	8.1	.3	19.0	6.0
		New England	103, 104, 105, 106, 107, 108.	.25	5.6	115	20.8	8.8	.4	20.5	6.7

TABLE 3.—*Average construction data of brick walls*—Continued

B. WALLS OF SERIES 2—Continued

Type of wall	Mortar	Kind of brick	Wall Nos.	Average thickness of mortar joints	Rate of building wall	Number of brick laid per hour	Brick per square foot of wall surface	Mortar materials used (pounds per square foot of wall surface)			
								Cement	Lime	Sand (dry)	Water
				Inch	*Sq. ft. hr.*						
8-inch all-rolok	Cement-lime	Mississippi	49, 50, 51	0.43	9.1	84	9.2	1.6	0.7	7.4	2.9
		New England	109, 110, 111	.35	8.5	87	10.2	1.8	.8	8.6	2.3
	Cement	Mississippi	52, 53, 54	.42	10.4	97	9.4	2.8	.1	6.5	2.1
		New England	112, 113, 114	.36	9.0	92	10.2	3.1	.1	7.1	2.3
12-inch all-rolok	Cement-lime	Mississippi	55, 56, 57	.44	7.4	103	13.8	2.3	1.0	10.9	3.4
		New England	115, 116, 117	.36	6.6	100	15.1	2.6	1.1	12.0	3.3
	Cement	Mississippi	58, 59, 60	.44	7.1	99	14.0	4.7	.2	11.1	3.6
		New England	118, 119, 120	.40	5.8	87	14.9	4.8	.2	11.3	3.6
8-inch all-rolok in Flemish bond	Cement-lime	Mississippi	61, 62, 63	.43	10.6	99	9.3	1.6	.7	7.5	2.4
		New England	121, 122, 123	.40	8.7	89	10.2	1.6	.7	7.6	2.3
	Cement	Mississippi	64, 65, 66	.44	10.3	96	9.4	3.0	.1	7.0	2.0
		New England	124, 125, 126	.39	8.6	87	10.1	3.1	.1	7.3	2.5
12-inch all-rolok in Flemish bond	Cement-lime	Mississippi	67, 68, 69	.45	6.9	100	14.5	2.2	.9	10.4	3.2
		New England	127, 128, 129	.43	6.2	99	16.0	2.5	1.1	11.8	3.8
	Cement	Mississippi	70, 71, 72	.44	7.9	115	14.6	4.7	.2	10.9	3.6
		New England	130, 131, 132	.42	5.3	85	16.0	4.5	.2	10.5	3.3
8-inch rolok-bak	Cement-lime	Mississippi	73, 74, 75	.41	9.7	103	10.7	1.8	.7	8.3	2.7
		New England	133, 134, 135	.32	7.7	89	11.6	2.0	.9	9.3	2.9
	Cement	Mississippi	76, 77, 78	.46	8.3	88	10.5	3.4	.1	7.9	2.5
		New England	136, 137, 138	.33	6.5	75	11.6	3.7	.2	8.8	2.8
12-inch rolok-bak (heavy duty)	Cement-lime	Mississippi	79, 80, 81	.44	7.7	124	16.1	2.8	1.2	13.4	4.0
		New England	139, 140, 141	.33	6.3	109	17.3	2.8	1.2	13.4	4.4
	Cement	Mississippi	82, 83, 84, 85, 86	.46	7.0	111	15.9	4.7	.2	10.9	3.5
		New England	142, 143, 144, 145, 146	.33	5.2	92	17.6	5.8	.3	13.5	4.0
12-inch rolok-bak (standard)	Cement	Mississippi	87	.50	5.6	80	14.3	5.5	.2	12.8	4.9
		New England	147	.28	4.9	73	14.8	5.2	.2	12.2	4.2
4-inch "economy"	Cement-lime	Mississippi	88, 89, 90	.42	8.5	65	7.6	2.1	.9	9.6	3.0
		New England	148, 149, 150	.29	7.3	60	8.2	2.1	.9	9.8	2.8
	Cement	Mississippi	91, 92, 93	.44	8.3	62	7.5	3.4	.1	8.0	2.8
		New England	151, 152, 153	.27	7.2	60	8.2	3.8	.2	9.0	2.6

(2) MATERIALS USED.—Table 3 also shows the amounts of the various mortar materials used for each square foot of wall surface. The amount of water used in the mortar is also reported. The number of bricks per square foot of wall surface was obtained by dividing the counted number of bricks in the wall by the area of the wall surface.

(3) COMPARATIVE CONSTRUCTION DATA FOR DIFFERENT TYPES OF WALLS.—In order to study the comparative construction data for different types of walls, only the walls built of Mississippi and New England brick will be considered, since no hollow walls were built of either the Chicago or the Detroit brick. In order to limit the variables still further, only walls of series 2 will be considered first. These walls were all built by one mason and included 60 walls each of Mississippi and New England brick. It should be remembered that the solid walls of this group had full horizontal and vertical mortar joints.

Although two different mortars were used, it is possible to bring them to a common basis for comparing the quantities of mortar materials by a study of the amounts of sand. This is permissible, since each mortar is essentially 1 part of cementing materials to 3 parts of sand.

Since the same number of walls was built of each kind of brick, the number of bricks per square foot of wall surface has been averaged for all the walls of one type and these values are given in Table 4 (A).

The rate of building will, of course, vary with the mason, the kind of structure, and other factors. The data given in Table 4 (A) were obtained with walls which were all of the same size, were built in the same laboratory and by the same mason and helper. A comparative study of building time can, therefore, be made from these data directly, although it should be remembered that there were no openings, jambs, or corners which might make some difference in the respective rates of building the different types of walls.

The 8-inch and the 12-inch solid walls have been used as the basis for a comparison of the materials and the time required for building the different types of walls. Since it seems more logical to compare the time required to build walls of equal size rather than the rate of building, the time ratios, which are proportional to the reciprocals of the rate of building, are also given. These ratios are plotted in Figure 14.

TABLE 4.—*Average construction data of solid and hollow walls of brick*

(A) WALLS OF SERIES 2

COMPARISON WITH 8-INCH SOLID WALLS

Type of walls	Number of walls	Sand	Brick per square foot	Rate of building	Ratios to solid walls			
					Sand	Brick	Rate of building	Time
		Lbs./ft.[3]		*Sq.ft./hr.*				
8-inch solid	12	13.5	13.0	7.4	1.00	1.00	1.00	1.00
8-inch all-rolok	12	7.4	9.8	9.2	.55	.75	1.24	.81
8-inch A. r. F. b.[1]	12	7.4	9.7	9.6	.55	.75	1.30	.77
8-inch rolok-bak	12	8.6	11.1	8.0	.64	.86	1.08	.93
4-inch economy	12	9.1	7.9	7.8	.67	.61	1.05	.95
COMPARISON WITH 12-INCH SOLID WALLS								
12-inch solid	18	20.8	19.8	5.6	1.00	1.00	1.00	1.00
12-inch all-rolok	12	11.3	14.2	6.7	.54	.72	1.20	.83
12-inch A. r. F. b.[1]	12	10.9	15.3	6.6	.52	.77	1.18	.85
12-inch rolok-bak	18	12.6	16.5	6.3	.61	.83	1.12	.89
(B) WALLS OF SERIES 1								
COMPARISON WITH 8-INCH SOLID WALLS								
8-inch solid	1	11.8	11.25	17.4	1.00	1.00	1.00	1.00
8-inch all-rolok	1	7.4	8.73	19.2	.63	.78	1.10	.91
8-inch A. r. F. b.[1]	1	12.2	8.90	17.5	1.03	.79	1.00	1.00
8-inch rolok-bak	1	8.8	10.00	20.5	.74	.89	1.18	.85

[1] All-rolok-in-Flemish-bond type of wall.

Tables 4 (A) and Figure 14 show that there is a considerable saving in brick and mortar materials in all the hollow walls as compared to solid walls of the same thickness. The all-rolok walls and the all-rolok walls in Flemish bond show a saving of at least 45 per cent in mortar materials and of about 25 per cent in the number of brick required. The rolok-bak walls, on the average, show savings of about 40 per cent in mortar materials and 15 per cent in brick. Of the eighteen 12-inch rolok-bak walls mentioned in Table 1, 16 were of the heavy-duty type and 2 of the standard type described in the reference. The time required to build the hollow walls is also less than for solid walls of equal thickness. Fewer brick are needed for the 4-inch "economy" walls than for the 8-inch hollow walls, but because of the back plastering the amount of mortar (per square foot of wall surface) was about the same as for the 8-inch hollow walls. On account of the time taken for plastering the back, the average amount of wall area built per hour was only 5 per cent more than with the solid 8-inch walls.

These walls, referred to in Table 4 (A) were built by a mason who was hired by the day, and they may be classed as construction under careful supervision. In order to have a comparison between this quality of work and work without careful supervision, the four walls (155

to 158) of series 1 may be considered. These were all 8-inch walls of series 1 built of Mississippi brick with cement mortar. The construction data for these walls are given in Table 4 (B).

(4) THICKNESS OF THE MORTAR JOINTS.—The average thickness of the horizontal mortar joints is given in Table 3. These values

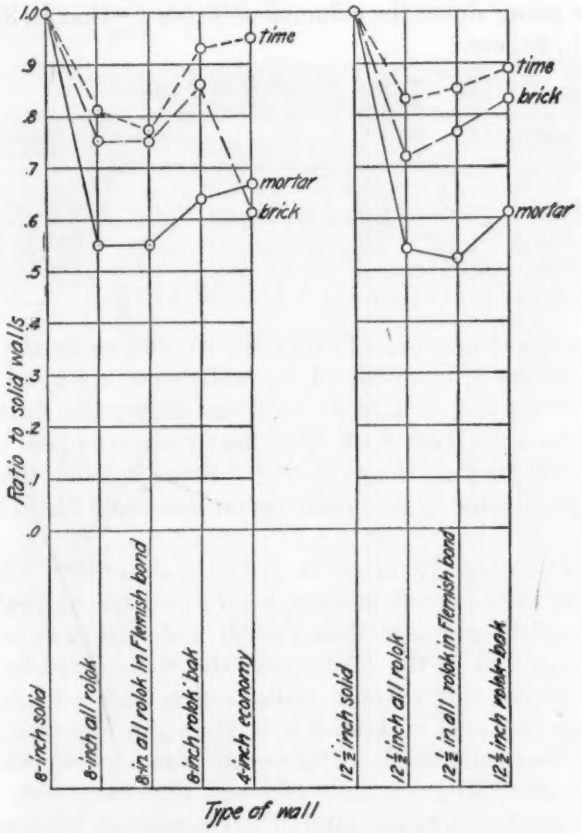

FIGURE 14.—*Comparative construction data of walls of series 2. The data from the 8-inch and 12-inch solid walls have been used as the basis of comparison*

were found by subtracting the total brick thickness (number of courses times average thickness of brick as given in Table 2) from the height of the wall and dividing by the number of mortar joints. The mortar joints in the walls of series 1 were much thicker than in those of series 2.

(f) AGING CONDITIONS

The walls remained in the laboratory, as shown in Figure 1, until they were tested.

(1) SCHEDULE OF BUILDING.—On account of the long time (more than one year) required for these tests, Table 5 is given to show the dates at which the walls were built and tested.

In order to minimize the effect of changes which might occur in curing conditions or change in workmanship, the walls 34 to 153 of Mississippi and New England brick, series 2, were built in the order shown by going down the columns of Table 1—that is, 34, 37, 40–91, 94–151, 35, 38, etc.

TABLE 5.—*Schedule of walls*

Series	Wall Nos.	Brick	Building started	Testing completed
1	1 to 17	Chicago	Apr. 4, 1926	June 21, 1926
2	19 to 33	Detroit	May 3, 1926	July 23, 1926
2	34 to 153	Mississippi and New England	May 27, 1926	Mar. 4, 1927
2	18	Chicago	July 31, 1926	Sept. 27, 1926
1	154 to 159	New England and Mississippi	Jan. 19, 1927	Mar. 22, 1927
2	160 to 167	Chicago	Aug. 19, 1927	Oct. 29, 1927
2	168	do	Sept. 1, 1927	Feb. 16, 1928

(2) THE LABORATORY.—The curing conditions in the laboratory, shown in Figure 1, in which all the walls were built and tested, was generally about the same as out of doors during the spring, summer, and autumn, since large doors were nearly always open. During the colder part of the year it was heated. Being indoors, the walls were, of course, protected from precipitation and from the direct rays of the sun.

(3) DAMP-CURED WALLS.—In order to determine whether brick walls, built with cement mortar, kept damp for several days after construction are stronger than similar walls allowed to age under normal conditions in the laboratory, the walls listed in Table 1 as "wetted" were built. These walls, which were all laid in cement mortar, were covered with burlap, as shown in Figure 15, as soon as they had been completed. The burlap was kept wet for one week after the walls had been built and was then removed. These wet walls were similar as to the kind of brick, mortar, workmanship, and size to an equal number of walls which were not covered with wet burlap, as may be seen in Table 1.

(g) AGE

The walls were tested from 57 to 62 days after construction, with the exception of wall 168, built of Chicago brick with cement mortar, which was tested when 169 days old for the purpose of exhibiting the test to a group of visitors.

(h) TESTING MACHINE

The walls were tested in the 10,000,000-pound capacity compression machine, shown in Figures 1 and 16. This machine is of the vertical type and is capable of testing specimens whose height does not exceed 25 feet and whose width in the clear does not exceed 6 feet.

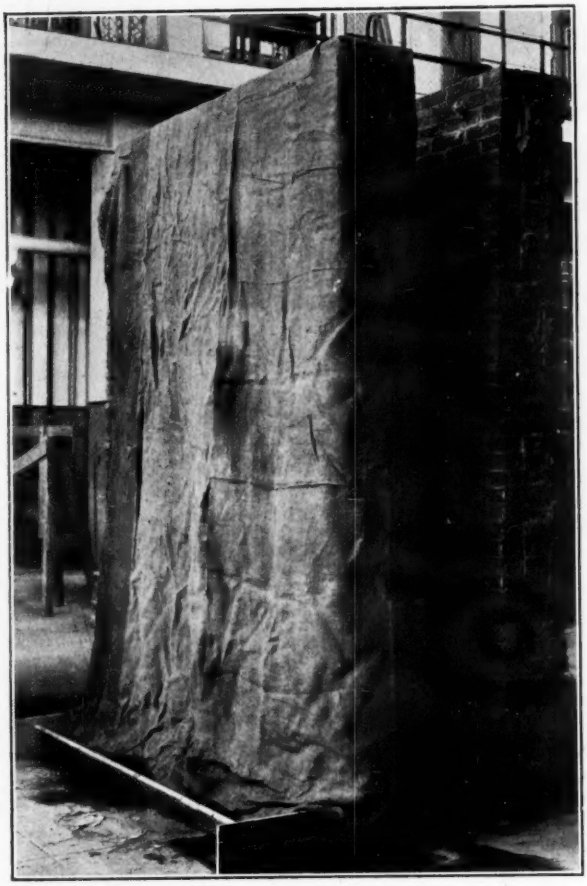

FIGURE 15.—*A wall covered with burlap for damp curing*

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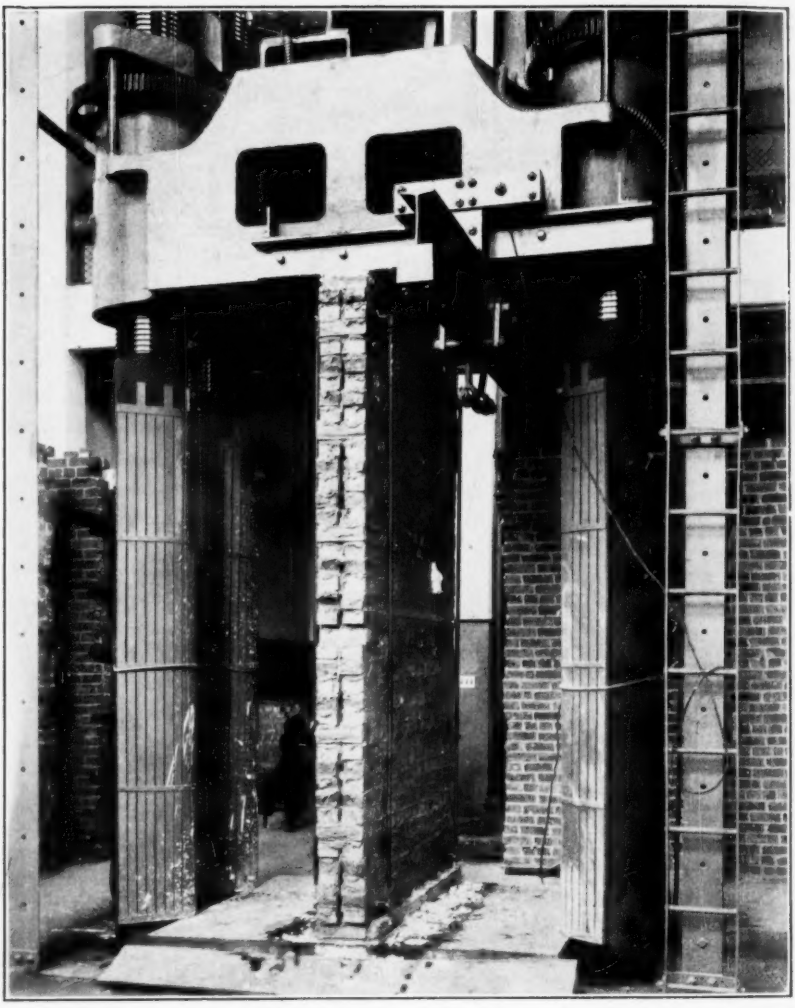

FIGURE 16.—*A wall in the 10,000,000-pound capacity testing machine ready for test*

The upper head during a test remains stationary, but for the purpose of adjusting the machine to the height of the specimen this head is moved by large nuts turning on the four 13½-inch diameter screws of the machine. These nuts are turned by a gearing mechanism which is driven by an electric motor placed on the head.

The lower platen, 6 feet square, rests on a spherical base of 5 feet radius which is mounted upon a vertically acting piston of 50 inches diameter and 24-inch stroke. There is attached to the bottom of this ram a guiding plunger 14 inches in diameter and 2 feet 5 inches long which fits into the large base casting of the testing machine and serves for proper centering of the parts.

The lower, or straining platen, is subject to the oil pressure in the cylinder, which, at the capacity of the machine, is approximately 5,000 lbs./in.^{2} The oil pressure communicates through auxiliary piping with a smaller piston of 5$^9/_{16}$ inches diameter. This piston has a "knife-edge" bearing on the main lever, *M*, of the testing machine lever system. (See fig. 17 for reference to the various parts by letters.) The ratio of the areas of the large and small piston is approximately as 80:1, the weighing lever, *L*, being graduated up to 2,000,000 pounds to read the actual load on the specimen. For loads greater than 2,000,000 pounds four weights, *W*, are provided, which may be placed on the end of the lever as desired. Each of these weights when attached to the end of the lever has a moment about the balance point *B* of the lever equal to that of the poise when it is at the 2,000,000-pound graduation, *2 M*. Thus, if one weight is used and the poise, *P*, indicates a given load, the force on the specimen is equal to 2,000,000 pounds plus the poise reading.

The pressure in the cylinder of the machine is obtained by means of a triple plunger oil pump, *O*, having an air dome, *A*, for equalizing the pulsations of the three pistons. The pump is belt driven by an electric motor, *E*. The piping from the pump leads to the bottom of the cylinder and is directed downward toward its base, while the piping which leads to the weighing piston is taken from the top of the cylinder, as far as possible from the other pipe, and where there is the least disturbance.

The passage of oil from the pump is controlled by two valves, *V*, and the system is protected from dangerous pressures by an automatic overload relief valve. The oil can also be passed directly from the pump back to the reservoir by means of a hand-controlled relief valve, *R*. The speed of the lower platen may be varied in the following manners: By varying the lengths of stroke of the pump pistons through the handwheel, *H;* by operating a by-pass needle valve, *N*, which controls the size of the passage in the valve block; by manipulating the globe valves, *V*, or the relief valve, *R;* or by varying the operating speed of the motor through the motor-controller switch.

The speed of the main piston may in this manner be varied from zero to ⅝ inch per minute at no load.

(i) METHOD OF TESTING

The walls were tested in compression under central loading. For these tests the channel at the base of the wall was bedded in plaster of Paris. The lower platen was then tilted, if necessary, until the wall was plumb and the top of the wall was nearly parallel to the lower surface of the upper head of the testing machine. A cap of plaster of Paris (calcined gypsum) was then spread on the top of the wall and the upper head lowered until the space between it and the wall was filled with plaster. The gypsum was allowed to set for at least an hour before the test was begun.

Vertical compressometers having a gage length of about 100 inches were attached near each corner, as shown in Figure 16. Horizontal extensometers were also fastened along the length on each side at mid height of the wall. These had a gage length of about 48 inches. The dial micrometers were graduated to 0.001 inch, and readings were taken at each 50 or 100 lbs./in.^{2} increment of load on the wall. The vertical speed of the lower platen was about 0.06 inch per minute during the application of load. When readings were being taken, the load was held constant.

4. WALLETTES

One hundred and twenty-nine wallettes or small walls, each about 18 inches long and 34 inches high, were built, which differed only in size from the wall of the same number. The walls and wallettes of the same number corresponded as to brick, mortar, type, curing conditions, and workmanship. No wallettes of the "economy" type were built, since that design is not adapted for specimens of wallette size. A group of wallettes is shown in Figure 18. The wallettes were built to determine whether walls smaller than the 6 by 9 foot specimens possessed compressive strengths which had a definite relation to those of the wall specimens. All but the strongest wallettes were tested in a 600,000-pound capacity universal testing machine using a spherical bearing, as shown in Figure 19. One of the wallettes (No. 104) tested in the 600,000-pound capacity machine could not be broken. It was then retested in the 10,000,000-pound machine. All other wallettes of this type which were tested later were then tested in the 10,000,000-pound machine.

IV. RESULTS OF THE TESTS WITH DISCUSSION

1. BRICK

The results of the tests of the single bricks are given in Table 6. Each average value, except those for shearing strength, is the average result from 50 tests.

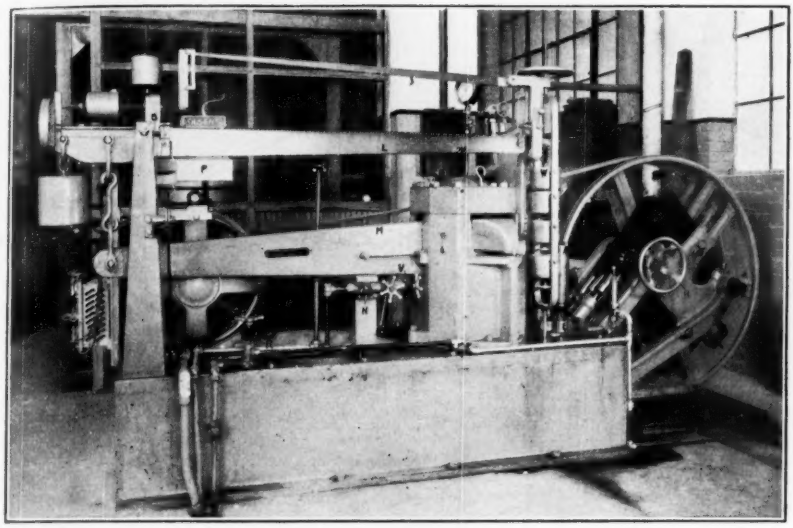

FIGURE 17.—*Pump and weighing mechanism of the 10,000,000-pound capacity testing machine*

FIGURE 18.—*A group of wallettes of series 2, built of Detroit brick*

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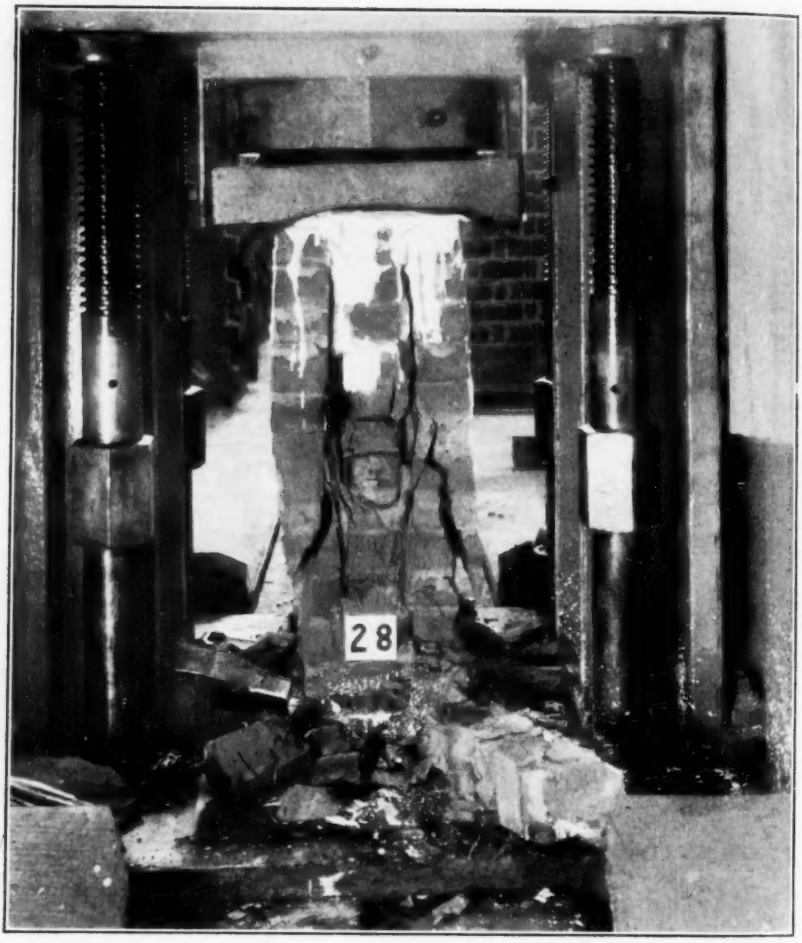

FIGURE 19.—*A wallette in the 600,000-pound capacity testing machine*

Wallette 28, of series 2, built of Detroit brick, laid in cement mortar. The maximum stress withstood by this specimen was 1,605 lbs./in.^{2}.

TABLE 6.—*Physical properties of the brick*

Kind of brick	Value	Absorption		Modulus of rupture			Compressive strength						Tensile strength	Shearing strength
							Flatwise			Edgewise				
		5-hour boiling	48-hour immersion	Flatwise	Flatwise (wet)	Edgewise	Whole brick (dry)	Half brick (dry)	Half brick (wet)	Whole brick (dry)	Half brick (dry)	Half brick (wet)		
		Per cent	*Per cent*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*
Chicago	Maximum	23.0	22.0	2,420	2,830	2,990	4,820	4,720	6,120	6,660	5,860	6,070	750	1,445
	Minimum	10.5	4.9	520	380	420	2,190	2,140	2,430	1,330	1,640	2,410	204	940
	Average	16.5	11.7	1,225	1,470	1,340	3,460	3,280	3,670	2,810	3,350	3,620	417	[1] 1,100
Detroit	Maximum	25.5	22.5	1,062	972	1,055	4,850	5,950	4,320	4,360	4,230	6,560	332	1,500
	Minimum	19.4	16.4	422	327	226	2,270	2,110	1,740	2,690	2,410	1,680	123	810
	Average	22.3	20.7	670	632	680	3,255	3,540	2,520	3,380	3,270	3,165	222	[1] 1,165
Mississippi	Maximum	25.1	21.8	1,540	1,390	1,480	6,460	6,510	7,100	5,760	7,330	5,630	513	2,190
	Minimum	18.4	12.3	324	441	387	2,590	2,390	1,740	1,460	2,320	2,160	148	1,155
	Average	21.7	16.7	820	750	760	3,625	3,410	3,520	3,200	3,625	3,620	317	[1] 1,590
New England	Maximum	14.9	11.9	2,330	3,540	2,340	14,160	12,270	11,830	16,400	15,500	18,750	1,160	4,255
	Minimum	3.1	2.4	940	818	448	5,180	5,380	3,710	5,380	6,390	5,510	325	2,460
	Average	9.2	6.9	1,550	1,400	1,640	9,420	8,600	6,990	10,300	11,470	11,020	601	[2] 3,550

[1] Average of 10 tests on half brick.

[2] Average of 4 tests on 1-inch thick cut slab.

The number 50 represents a complete sampling of the shipment. While most determinations were checked by two or more independent samplings and tests, for the purposes of this paper a particular set of samples was selected and the others disregarded. On the basis of the large number of tests made, it can be stated that the strengths of a given lot as determined by averages of 50 specimens may differ by as much as 10 per cent. Hence, small differences, such as appear between the wet and dry compressive and transverse strengths of the Chicago brick, for example, should be disregarded, being within the variations due to sampling alone.

While, in general, there is a fair correlation between the different measures of strength, comparing one kind of brick with another, certain divergencies are evident which may well have an important effect on masonry strength. This will be discussed later in the paper. For the present, attention is called to Table 7, where the ratios of these various physical properties are given.

Disregarding comparisons of strength wet with strength dry, and considering the mean deviation divided by the mean as given in Table 7 as a measure of agreement, the most constant ratios are those of tensile strength to modulus of rupture. The ratio of modulus of rupture to shearing strength shows the greatest deviation.

TABLE 7.—*Ratios of various physical properties of brick*

Kind of brick	Absorption: 48-hour cold / 5-hour boiled	Compressive stength of half brick: Edge, dry / Flat, dry	Compressive stength of half brick: Flat, wet / Flat, dry	Modulus of rupture (flat, dry) / Compressive strength of half (flat, dry)	Tensile strength / Modulus of rupture (flat, dry)	Modulus of rupture (flat, wet) / Modulus of rupture (flat, dry)	Modulus of rupture (flat, dry) / Shearing strength	Tensile strength / Compressive strength of half (flat, dry)	Shearing strength / Compressive strength of half (flat, dry)
1	2	3	4	5	6	7	8	9	10
Chicago	0.71	1.02	1.12	0.37	0.34	1.29	1.11	0.13	0.34
Detroit	.93	.92	.71	.19	.33	.94	.58	.06	.33
Mississippi	.77	1.06	1.03	.24	.39	.92	.52	.09	.47
New England	.75	1.33	.81	.18	.39	.90	.44	.07	.41
Mean deviation / Mean	.08	.11	.17	.24	.08	.10	.34	.22	.14

A study of Tables 6 and 7 will show that the Chicago brick is different from the other three kinds in that its ratio of modulus of rupture and of tensile strength to compressive strength and to shearing strength is markedly higher than are the corresponding strength ratios for the other three bricks, as may be noted in columns 5, 8, and 9 of Table 7. This is possibly explained by the structure of the brick, end cut and laminated, which gives the effect of a bundle of fibers running lengthwise of the brick.

Of the other three kinds of brick, two represent the soft-mud and one the dry-press method of manufacture.

In the original plan for these tests it was the intention to use bricks corresponding to the four grades in the American Society for Testing Materials' Specification for Building Brick (C21–24). On the basis of the average values here given these brick would classify as follows:

	Absorption, 5-hours boiling	Modulus of rupture flatwise	Compressive strength halves on edge
Chicago	Medium	Vitrified	Medium.
Detroit	Soft	Hard	Do.
Mississippi	do	do	Hard.
New England	Hard	Vitrified	Vitrified.

Under the American Society for Testing Materials new Tentative Specification for Building Brick (made from clay or shale) (C62–28T) these brick classify as follows:

	Compressive strength halves flatwise	Modulus of rupture flatwise
Chicago	B	A
Detroit	B	A
Mississippi	B	A
New England	A	A

For both these classifications it is provided that the grading "shall be determined by the results of the tests for that requirement in which it is lowest unless otherwise specified * * *."

Figures 20, 21, 22, and 23 give the distribution of the individual tests, averages of which are given in Table 6. The 50 tests in each group are not enough to give a satisfactory distribution, but these graphs give an idea of the variability of the brick.

2. MORTAR

The average results of the tests of the mortar specimens are given in Table 8.

TABLE 8.—*Compressive strength of mortar specimens*

[Cylinders 2 inches in diameter, 4 inches long]

REPRESENTING WALLS 1 TO 18 AND 160 TO 162

Mortar	Proportions (by volume)	Strength	
		Cured wet	Cured dry
		Lbs./in.²	*Lbs./in.²*
Lime	1¼ L: 3S		90
Cement-lime	1 C: 1¼ L: 6S	1,070	500
Cement	1 C: 3S	3,580	1,460

REPRESENTING WALLS 19 TO 159 AND 163 TO 168

Cement-lime	1 C: 1 L: 6S	1,100	750
Cement	1 C: $\frac{1}{10}$ L: 3S	3,260	1,950

3. WALLS

(a) BASIS OF COMPUTATIONS

The sectional area of the wall was obtained by multiplying the average thickness by the length (72 inches). All wall stresses, except some of those in Table 10, were obtained by dividing the load by this measured (not nominal) gross area. The stresses in the hollow walls are also based on the gross measured areas.

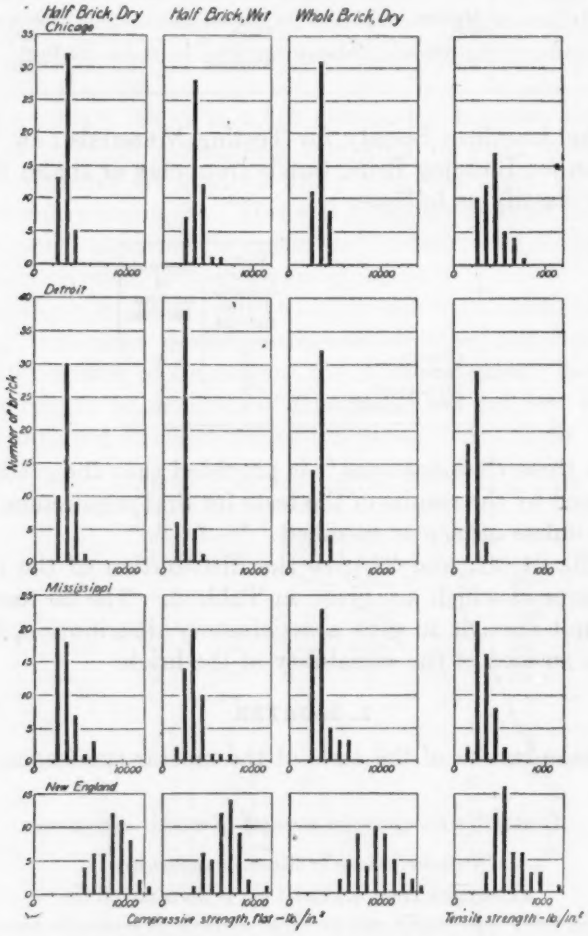

FIGURE 20.—*Results of the tests on brick*

Compressive strength, flat, half brick, half brick dry, half brick wet, and whole brick dry, and tensile strength

(b) DEFORMATION OF THE WALLS

(1) STRESS-STRAIN CURVES.—The average stress-strain curves of the solid walls of series 1 built of Chicago brick are shown in Figure 24. These curves show the differences in stiffness due to differences in the mortar. Both the average vertical compression and the horizontal extension of the wall at mid height have been plotted against the com-

pressive stress. The horizontal extension is much less than the vertical compression, but no constant relation between them, such as the nearly constant Poisson's ratio for some metals, appears to exist. The ratio of extension to compression, however, increases with increase in stress.

The relative stiffness of the different types of walls is shown in Figure 25. This shows average stress-strain curves for the 8-inch

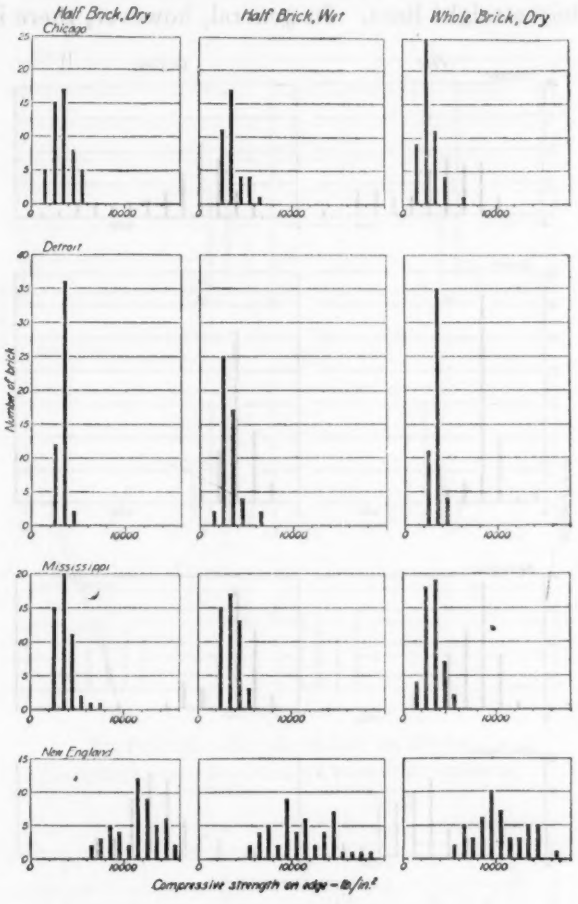

FIGURE 21.—*Results of the tests on brick*

Compressive strength on edge, half brick dry, half brick wet, and whole brick dry

walls of series 2 of Mississippi brick laid in cement mortar. These curves for the different types of walls are typical of those found in the other groups of walls. The solid walls deform less than the hollow walls and the different types of hollow walls appear to deform about equally for equal stresses.

Average stress-compression curves for 12-inch solid walls of series 2 built with cement mortar and of different kinds of brick are shown in

Figure 26. Since the same mortar mixture was used for all of these walls the differences in stiffness are due in large part to differences in the properties of the brick, although differences in the thickness of the mortar joints doubtless had an influence.

(2) SECANT MODULUS OF ELASTICITY.—For the walls laid in cement-lime and cement mortars the stress-strain curves are, for low stresses, approximately straight lines. In general, however, there is no value

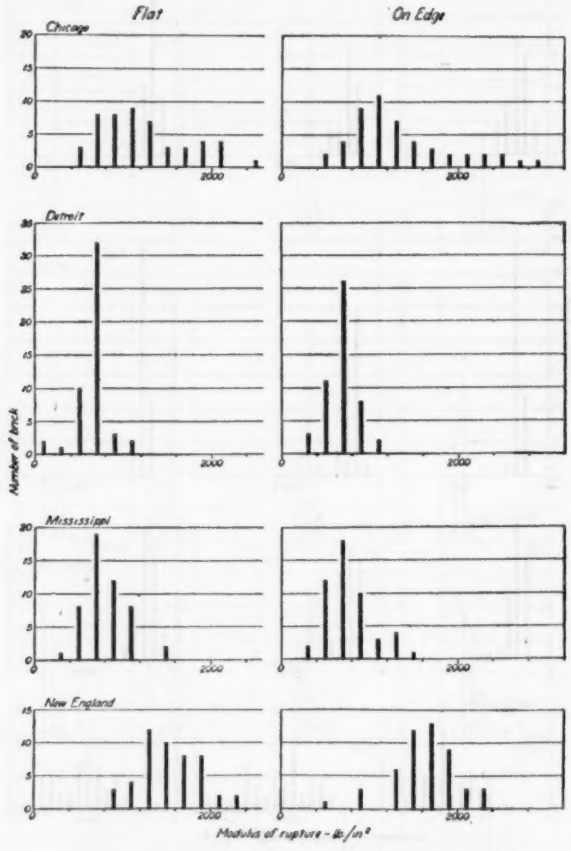

FIGURE 22.—*Results of tests on brick*

Modulus of rupture, flat and on edge

for a modulus of elasticity which is constant over a large stress range. For computing the shortening of a wall under the first application of working loads, the secant modulus of elasticity, obtained by dividing the stress by the corresponding value of the compressive strain, may be of use. These values are given in Table 9. The stress ranges are—

0 to 125 lbs./in.² for lime mortar,
0 to 200 lbs./in.² for cement-lime mortar, and
0 to 250 lbs./in.² for cement mortar.

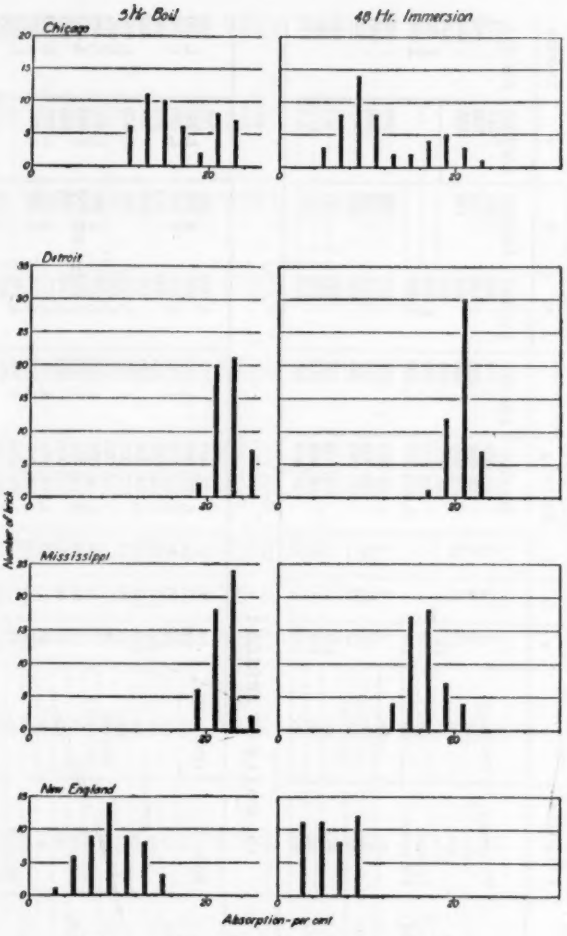

FIGURE 23.—*Results of tests on bricks*
Absorption per cent, 5-hour boil and 48-hour cold immersion

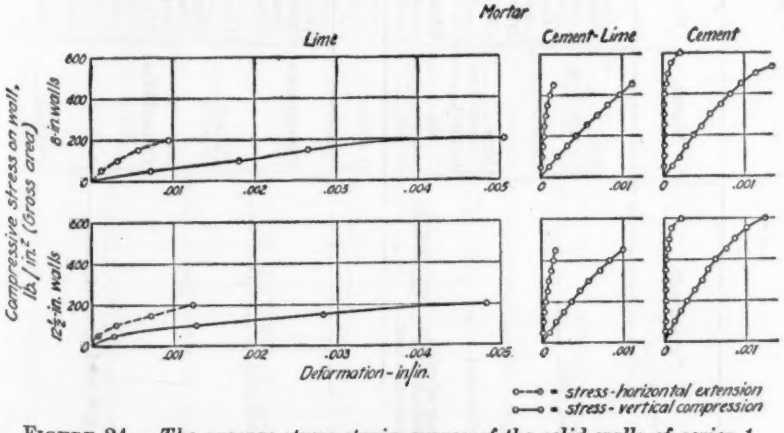

FIGURE 24.—*The average stress-strain curves of the solid walls of series 1 built of Chicago brick*

TABLE 9.—*Results of compressive tests of brick walls*

(A) WALLS OF SERIES 1

Type of wall	Mortar	Kind of brick	Workmanship (type of bed joints)	Curing conditions	Wall Nos.			Average secant modulus of elasticity	Average stress at first crack	Wall strength			
					a	b	c			a	b	c	Average
								Lbs./in.²	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*
8-inch solid	Lime	Chicago	Furrowed	Ordinary	1	2	3	54,000	200	255	250	315	275
	Cement-lime	do	do	do	7	8	9	459,000	520	575	620	590	595
	Cement	do	do	do	13	14	15	554,000	640	660	750	580	665
		Mississippi	do	do	155			493,000	870	870			870
		do	Spread	do	159			974,000	1,480	1,480			1,480
		New England	Furrowed	do	154			2,040,000	1,500	2,030			2,030
12-inch solid	Lime	Chicago	do	do	4	5	6	69,600	210	295	350	250	300
	Cement-lime	do	do	do	10	11	12	556,000	510	580	575	580	580
	Cement	do	do	do	16	17		686,000	600	655	655		655
8-inch all-rolok	do	Mississippi	do	do	156			379,000	335	440			440
8-inch all-rolok in Flemish bond	do	do	do	do	157			509,000	270	535			535
8-inch rolok-bak	do	do	do	do	158			453,000	485	745			745

(B) WALLS OF SERIES 2

8-inch solid	Cement-lime	Detroit	Spread	Ordinary	19	20	21	638,000	515	1,060	905	760	910
		Mississippi	do	do	34	35	36	1,031,000	1,125	965	1,175	1,340	1,160
		New England	do	do	94	95	96	2,049,000	1,165	1,785	1,875	1,710	1,790
		Chicago	do	do	160	161	162	1,041,000	865	800	870	965	880
		do	do	do	163	164	165	1,014,000	830	885	925	755	855
	Cement	Detroit	do	do	22	23	24	727,000	790	1,305	895	1,050	1,080
		do	do	Wetted	33			767,000	610	1,055			1,055
		Mississippi	do	Ordinary	37	38	39	1,300,000	1,270	1,335	1,405	1,405	1,380
		New England	do	do	97	98	99	2,360,000	1,750	2,040	2,950	2,915	2,635
12-inch solid	Cement-lime	Detroit	do	do	25	26	27	727,000	590	1,050	940	965	985
		Mississippi	do	do	40	41	42	1,288,000	1,155	1,375	1,305	1,225	1,300
		New England	do	do	100	101	102	2,461,000	1,100	1,815	1,990	1,855	1,890
		Chicago	Shoved	do	18			1,350,000	1,165	1,165			1,165
		do	Spread	do	166	167		1,060,000	875	890	1,080		985
		do	do	169 days old	168				1,065	1,200			1,200
	Cement	Detroit	do	Ordinary	28	29	30	935,000	800	1,165	1,345	1,115	1,210
		do	do	Wetted	31	32		809,000	665	1,040	1,165		1,105
		Mississippi	do	Ordinary	43	44	45	1,538,000	1,390	1,710	1,855	1,350	1,640
		do	do	Wetted	46	47		1,945,000	1,380	1,305	1,875		1,590
		do	Shoved	Ordinary	48			1,082,000	1,200	1,465			1,465
		New England	Spread	do	103	104	105	2,652,000	2,310	2,440	3,230	2,695	2,790
		do	do	Wetted	106	107		2,455,000	1,750	1,750	3,270		2,510
		do	Shoved	Ordinary	108			2,024,000	2,530	2,720			2,720

		New England	Spread	do	103	104	105	1,682,000	1,200	1,465			1,465
		do	do	Wetted	106	107		2,652,000	2,310	2,440	3,230	2,695	2,790
		do	Shoved	Ordinary	108			2,455,000	1,750	1,750	3,270		2,510
								2,024,000	2,530	2,720			2,720
8-inch all-rolok	Cement-lime	Mississippi	Spread	do	49	50	51	709,000	600	745	655	890	765
		New England	do	do	109	110	111	1,103,000	415	1,055	780	795	875
	Cement	Mississippi	do	do	52	53	54	883,000	785	850	735	1,175	920
		New England	do	do	112	113	114	1,209,000	430	1,005	1,065	795	955
12-inch all-rolok	Cement-lime	Mississippi	do	do	55	56	57	687,000	565	645	725	750	705
		New England	do	do	115	116	117	1,105,000	450	805	785	640	740
	Cement	Mississippi	do	do	58	59	60	681,000	665	795	745	870	800
		New England	do	do	118	119	120	1,217,000	665	775	935	895	870
8-inch all-rolok in Flemish bond	Cement-lime	Mississippi	do	do	61	62	63	743,000	545	800	750	695	750
		New England	do	do	121	122	123	1,199,000	600	555	745	610	640
	Cement	Mississippi	do	do	64	65	66	738,000	530	825	720	855	800
		New England	do	do	124	125	126	1,712,000	630	680	925	720	775
12-inch all-rolok in Flemish bond	Cement-lime	Mississippi	do	do	67	68	69	739,000	485	570	640	810	675
		New England	do	do	127	128	129	1,108,000	575	890	900	700	830
	Cement	Mississippi	do	do	70	71	72	804,000	500	550	660	920	710
		New England	do	do	130	131	132	1,422,000	605	940	1,005	880	940
8-inch rolok-bak	Cement-lime	Mississippi	do	do	73	74	75	857,000	810	950	905	965	940
		New England	do	do	133	134	135	1,151,000	530	815	1,155	680	880
	Cement	Mississippi	do	do	76	77	78	859,000	905	925	890	950	920
		New England	do	do	136	137	138	2,074,000	910	1,270	1,245	1,105	1,205
12-inch rolok-bak (heavy-duty)	Cement-lime	Mississippi	do	do	79	80	81	833,000	515	775	830	950	850
		New England	do	do	139	140	141	1,316,000	600	1,150	830	910	965
	Cement	Mississippi	do	do	82	83	84	782,000	755	1,035	835	955	940
		do	do	Wetted	85	86		866,000	650	1,025	905		965
		New England	do	Ordinary	142	143	144	1,694,000	775	1,635	1,525	1,610	1,590
		do	do	Wetted	145	146		1,803,000	740	1,400	1,250		1,325
12-inch rolok-bak (standard)	Cement	Mississippi	do	Ordinary	87			749,000	985	1,010			1,010
		New England	do	do	147			1,633,000	450	1,160			1,160
4-inch "Economy"	Cement-lime	Mississippi	do	do	88	89	90	1,155,000	1,375	1,370	1,365	1,565	1,435
		New England	do	do	148	149	150	1,826,000	1,235	1,960	1,975	1,880	1,940
	Cement	Mississippi	do	do	91	92	93	1,257,000	1,575	1,650	1,350	1,875	1,625
		New England	do	do	151	152	153	2,460,000	2,275	2,755	3,520	3,160	3,145

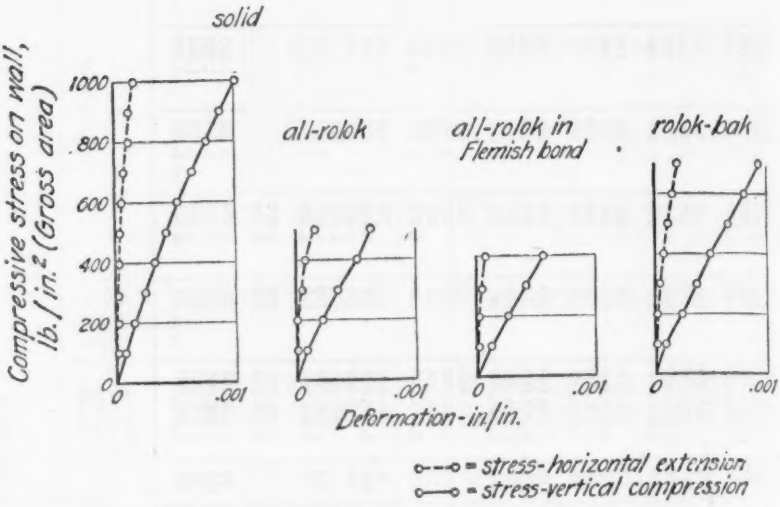

FIGURE 25.—*The average stress-strain curves for different types of 8-inch walls of series 2*

The walls were built of Mississippi brick laid in cement mortar

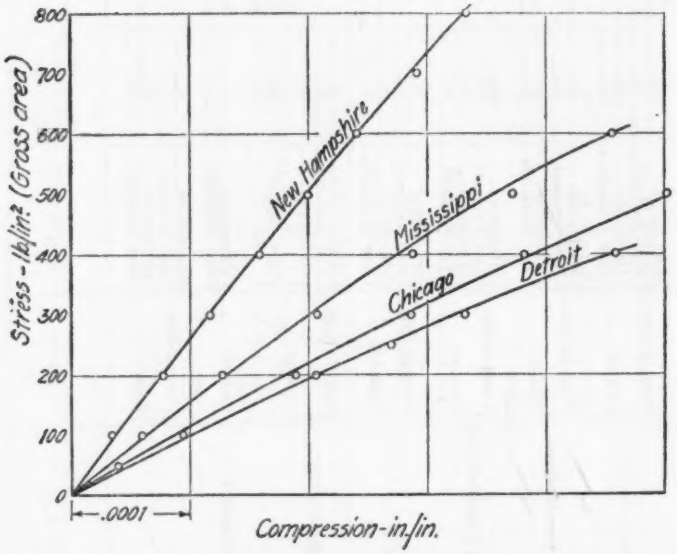

FIGURE 26.—*Average stress-compression curves for walls built of different kinds of brick*

The walls were 12-inch solid walls of series 2 laid in cement mortar

(3) PERMANENT SET.—The elastic behavior of these brick walls was found to be similar to that found for the masonry piers tested at Columbia University.[7] Upon release of load, a permanent set was found, and upon reapplication of the load, if the former load was not exceeded, the vertical deformation in the wall measured from its initial condition was only a little more than it was at the initial application of the load. Figure 27 shows the stress-compression curves for wall 42 which was subjected to repeated loadings. The slopes of the lines, which represent an increase of load, gradually decrease as higher loads are applied, although for the smaller stresses there is very little difference in the modulus of elasticity for consecutive loads. The deformation found on again attaining a certain load after a load release is slightly greater than the initial deformation, but upon proceeding to a higher load, the compression at that load appears to be equal to what it would have been if no release had taken place. In other words, the envelope of the stress-compression relations represented by the dotted line of Figure 27 with repeated loading appears to represent approximately the primitive stress-compression properties of the wall.

One wall in each group of three was subjected to a release of load test. Compressometer readings were taken as the load increased until the stress was reached for which the secant modulus of elasticity was computed. The stress was then reduced to 50 lbs/in.^{2}, readings were taken, and the load was reapplied. These second-loading moduli were in all cases larger than the corresponding values of the secant modulus of elasticity. For the lime-mortar walls the second loading moduli were more than three times as great as the primitive secant moduli, while with the other mortars the increase was from 10 to 50 per cent. Upon the release of load from a higher stress to 50 lbs./in.^{2}, a permanent set was always found. A typical stress-set curve is shown in Figure 27. The ordinates represent the stress from which release took place and the abscissas, the compression set at 50 lbs./in.^{2}, the stress to which the load was reduced. These set curves are fairly straight for the lower stresses, but for higher stresses the set increases more rapidly than the load.

(c) BEHAVIOR OF THE WALLS UNDER LOAD

In the solid lime-mortar walls (walls 1 to 6), as the load was increased the mortar was crushed and squeezed out of the horizontal beds. Soon after this occurred stretchers and headers broke, and at the maximum load more of the headers were broken and cracks appeared in many of the stretchers. These walls were all built of the end-cut Chicago brick and many of the stretchers split longitudinally.

[7] A. H. Beyer and W. J. Krefeld, Comparative Tests of Clay, Sand-Lime, and Concrete Brick Masonry, Bulletin No. 2, Department of Civil Engineering, Columbia University; 1923.

In the solid walls built with the cement-lime and the cement mortars longitudinal failure of the stretchers predominated in the walls

FIGURE 27.—*Stress compression and set curves for wall 42, a 12-inch solid wall of series 2, built of Mississippi brick, laid in cement-lime mortar*

of Chicago brick, while with the other kinds of brick, all of which were molded, the failure of the headers was characteristic. At the

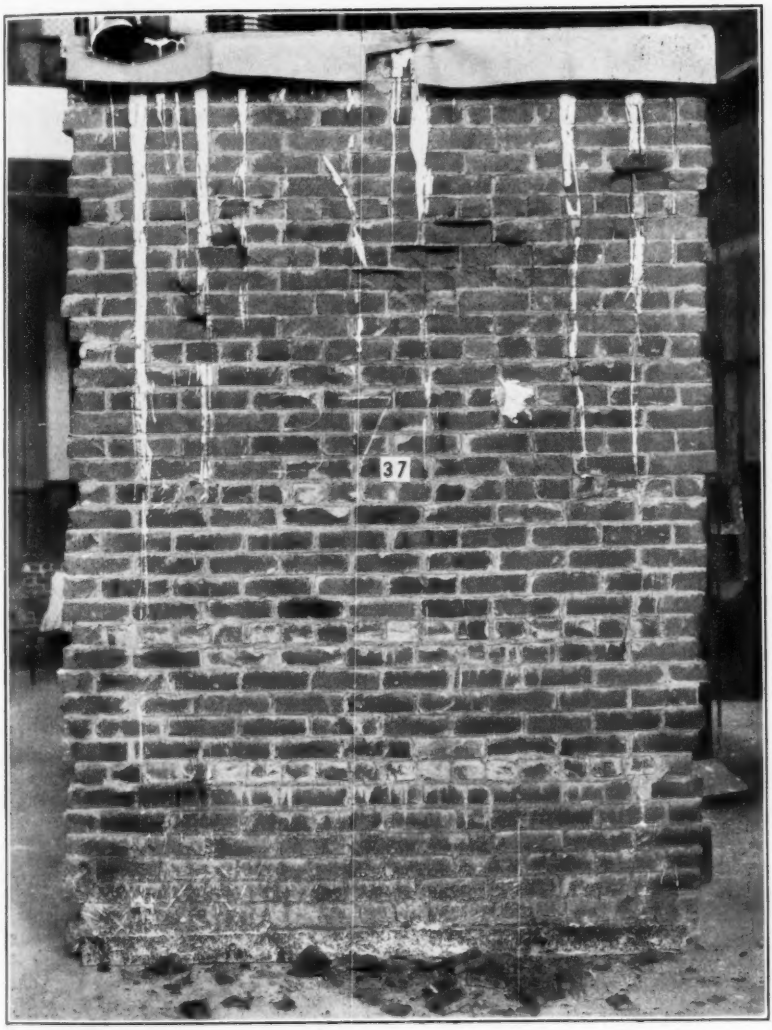

FIGURE 28.—*The 8-inch solid wall 37 of series 2, built of Mississippi brick, laid in cement mortar, after test*

The strength of this wall was 1,335 lbs./in.^{2}.

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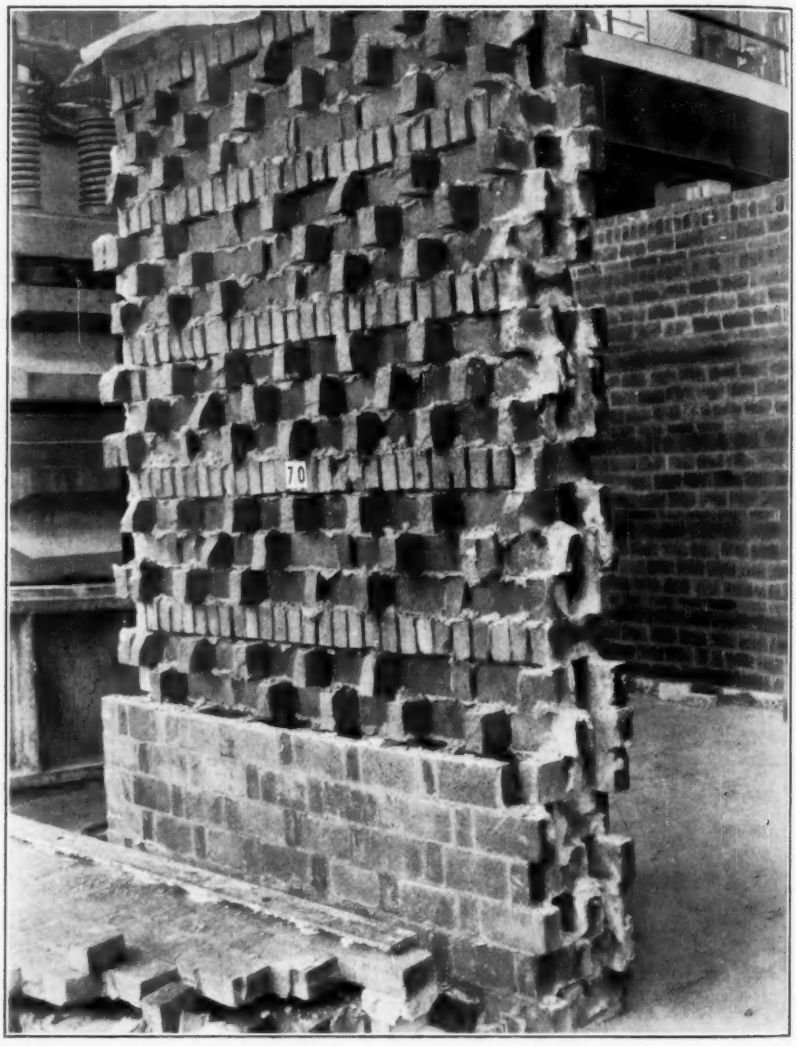

FIGURE 29.—*The 12-inch all-rolok in Flemish bond wall 70 of series 2, built of Mississippi brick, laid in cement mortar, after test*

The strength of this wall was 550 lbs./in.^{2}.

maximum load nearly all headers and many stretchers had broken, and in some cases, especially with the cement mortar, spalling of the brick and vertical cracks also occurred, as shown in Figure 28. No crushing of the mortar was observed except with the lime mortar.

The failure of the hollow walls was characterized by broken headers. Many of the 8-inch walls of the all-rolok and the all-rolok in Flemish bond types continued to take load until all the headers had been broken and total collapse took place. In the 12-inch walls of these types the rear withes often fell, as may be seen in Figure 29.

The failure of the rolok-bak walls was also characterized by header failures and the collapse of the rear rowlock withe.

In the "economy" walls the headers broke first, then the mortar plastering loosened, and finally stretcher cracks appeared. At the maximum load only the 4-inch withe was withstanding the load. The area of the pilasters has, however, been included in the area of the walls used to calculate the maximum stress.

The average values for the stresses when the first crack was seen are given in Table 9. There seems to be no definite relation between these stresses and the maximum stresses that the walls withstood, although there was, of course, a tendency for the load at failure to be larger if the load at first crack was large.

The loading was not continued after a marked decrease in the load showed that the maximum had been attained.

(d) COMPRESSIVE STRENGTH

The individual wall strengths, as well as the average value for any group of walls, are given in Table 9. The value of this table is largely as a compilation of data on the strength of brick walls, which differ as to the materials and the quality of workmanship used in their construction, and which may be duplicated in structures.

Since the selection of proper working stresses for brick masonry requires a knowledge of the principal factors that govern strength, the results given in Table 9 afford useful comparisons between the strength of the walls and the variables featuring their construction.

(e) THE COMPARATIVE STRENGTHS OF SOLID AND OF HOLLOW WALLS OF BRICK

In order to study the effect of design on the strength of brick masonry, the walls of series 2, alike in all respects except the type of wall built with spread mortar joints and aged under ordinary conditions, will first be considered.

The average results of the compressive tests of these brick walls are given in Table 10 and are shown graphically in Figures 30 and 31. Each value is the average for three similar walls.

The values of compressive strength, which are based on gross area, are the same as those in Table 9 and were obtained by dividing the maximum load on the specimens by the gross area. The net areas of the walls were calculated as the product of the actual width of the brick withes and the length of the walls. They are less than the gross areas because the thickness of the longitudinal vertical joint was not included. For the hollow walls these net areas represent the minimum area in compression and for the solid walls they represent the sums of the areas of the brick withes under compression. The gross and net areas are the same for the 4-inch economy wall.

TABLE 10.—*Average strength of the different types of brick walls of series 2*

Type of wall	Mississippi brick		New England brick	
	Compressive strength based on—			
	Gross area	Net area	Gross area	Net area
	Lbs./in.²	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*
CEMENT-LIME MORTAR				
8-inch solid	1,160	1,265	1,790	2,030
12-inch solid	1,300	1,450	1,890	2,180
8-inch all-rolok	765	1,345	875	1,570
12-inch all-rolok	705	1,270	740	1,350
8-inch all-rolok in Flemish bond	750	1,320	640	1,130
12-inch all-rolok in Flemish bond	675	1,220	830	1,500
8-inch rolok-bak	940	1,265	880	1,210
12-inch rolok-bak	850	1,280	965	1,480
4-inch economy	1,435	1,435	1,940	1,940
CEMENT MORTAR				
8-inch solid	1,380	1,515	2,635	2,980
12-inch solid	1,640	1,820	2,790	3,200
8-inch all-rolok	920	1,630	955	1,710
12-inch all-rolok	800	1,450	870	1,610
8-inch all-rolok in Flemish bond	800	1,405	775	1,380
12-inch all-rolok in Flemish bond	710	1,285	940	1,760
8-inch rolok-bak	920	1,240	1,205	1,670
12-inch rolok-bak	940	1,420	1,590	2,460
4-inch economy	1,625	1,625	3,145	3,145

The compressive strengths in pounds per square inch of the three types of solid walls are about equal. It is especially noteworthy that the thin 4-inch economy walls, when concentrically loaded, withstood as high compressive stresses as did the walls 8 and 12 inches thick.

For the walls built of either Mississippi or New England brick the solid specimens withstood greater loads and greater stresses, based on gross area, than did the hollow walls. If the wall strength is a function of the area in compression, as may reasonably be supposed, the strengths, based on net areas, should be the same for all walls built of the same kind of brick and laid in the same kind of mortar. This is apparently true for the walls of Mississippi brick,

as may be seen from Figure 30. The strength values listed under Mississippi brick, net area, in Table 10 are remarkably uniform for each mortar mixture, and it is apparent that the net areas of the walls built of Mississippi brick may be used as a basis of design for the hollow walls. These bricks were not warped, were fairly uniform in size, and had nearly perfectly rectangular cross sections.

The results of the tests of the hollow walls of New England brick, however, show that they do not have a constant compressive strength.

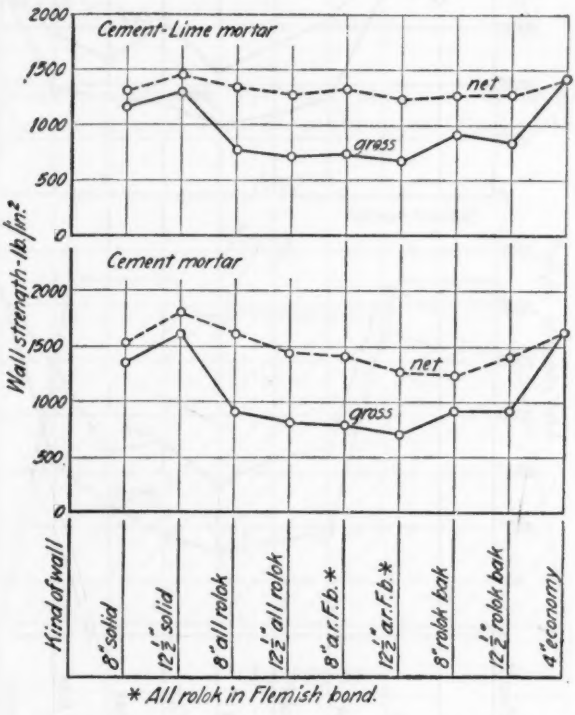

FIGURE 30.—*Average strength of the walls of series 2 built of Mississippi brick*

based on net area. Table 6 indicates that the various strength properties are from two to three times as much for the New England as for the Mississippi brick, while Table 10 shows that the solid walls of New England brick are considerably stronger than those of Mississippi brick. The strengths of the hollow walls are, however, not greatly different for the two kinds of brick.

The New England brick were not as regular in their shape as the other. The cross section of these brick was similar in shape to that shown in Figure 32, although the difference in width between top and bottom is much exaggerated. The difference in the top and bottom widths of these molded brick amounted to about 0.1 inch,

and it may be that this lack of a truly rectangular cross section affected the wall strength when the brick was laid on the narrow edge as in the hollow walls.

Since the hollow walls of the strong New England brick are not much stronger than those built of the Mississippi brick, it must be

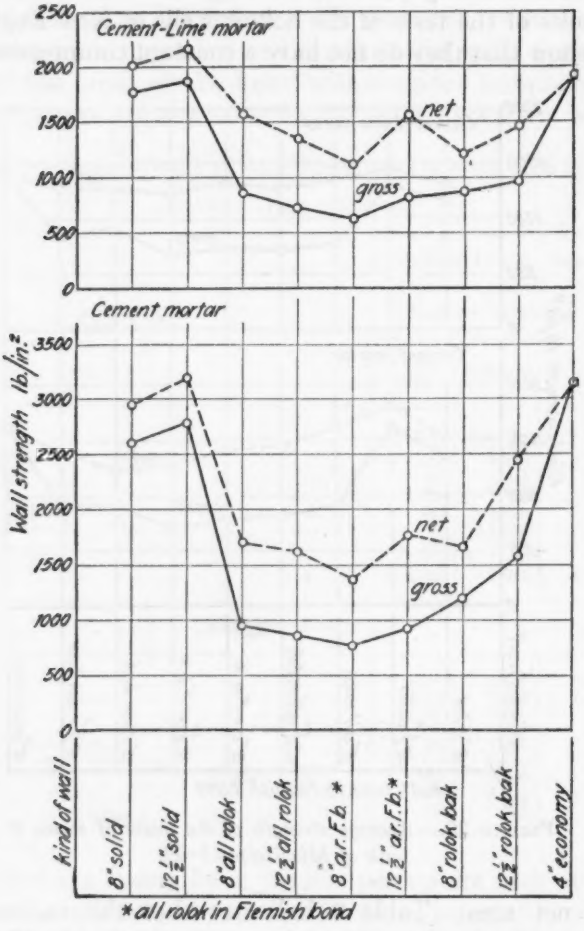

FIGURE 31.—*Average strength of the walls of series 2 built of New England brick*

concluded that the compressive and tensile strength and the modulus of rupture of the individual brick do not completely define the factors that have a determining influence on the strength of hollow masonry. Further research will be necessary before the strength of a hollow wall can be predicted from the strength of the brick and mortar.

In order to study the effect of type on wall strength when the walls were built with less care, those walls of series 1 listed in Table 11 will be considered.

TABLE 11.—*Strength of different types of walls of series 1*

[Brick, Mississippi; mortar, cement]

Type of wall	Wall No.	Wall strength based on—	
		Gross area	Net area
		Lbs./in.²	*Lbs./in.²*
8-inch solid	155	870	950
8-inch all-rolok	156	440	780
8-inch all-rolok in Flemish bond	157	535	940
8-inch rolok-bak	158	745	1,010

Since only one wall of each type was tested, the results are not very conclusive, but, in general, they show the same trend as those for the

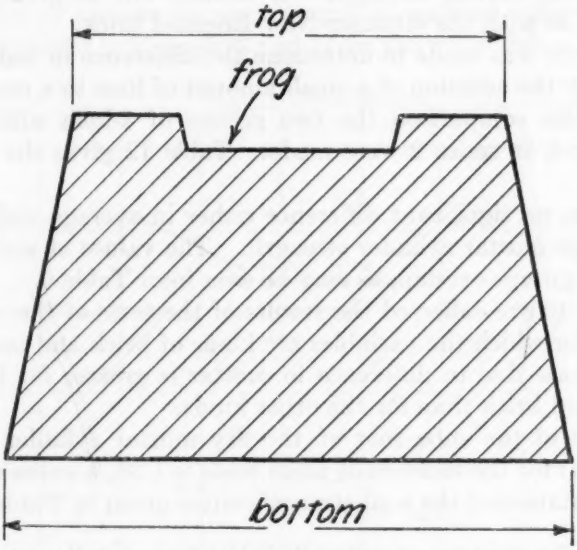

FIGURE 32.—*An exaggerated view of a cross section of an irregular brick*

walls of series 2 built of Mississippi brick. The solid wall withstood the greatest compressive stress, based on gross area, and the hollow walls were practically as strong as the solid, based on net area.

The walls of series 1 had lower strengths than those of series 2, but the values given in Table 11 show that the hollow walls of brick may be safely used for many construction purposes.

(f) THE EFFECT OF MORTAR ON THE STRENGTH OF WALLS OTHERWISE SIMILAR

In series 1 the tests of the solid walls of Chicago brick afford comparisons from which the effect of the mortar on wall strength can be determined. The three mortar mixtures had very different com-

pressive strengths as may be noted from Table 8. The strength of the solid walls (Table 9) varied about as the cube root of these mortar cylinder strengths. Although this is by no means to be taken as an exact relationship, the ratio of average wall strength to cube root of dry mortar cylinder strength is more constant for the three mixtures of mortar than any other simple relation which was tried.

The strengths of the mortar cylinders varied considerably from wall to wall with the same mixture, and only averages from a large number of cylinders can be said to have a significant value. In several of the groups of three walls which were alike in type of wall, mortar, workmanship, brick, curing conditions, etc., the difference in wall strength did not always follow in the same order as the differences in mortar cylinder strength. Furthermore, the increase in wall strength due to an increase in mortar strength was usually not as great with the Mississippi as with the stronger New England brick.

An attempt was made to determine the difference in wall strength produced by the addition of a small amount of lime to a cement mortar. For this comparison the two groups of 8-inch solid walls of Chicago brick in series 2 were made. Table 12 gives the results of these tests.

There was no significant difference either in average wall strength or in average mortar cylinder strength. The values of wall strength for the two groups overlap, as may be seen from Table 9.

In Table 13 are collected the results of the tests of the solid walls of series 2 for which the variables are kinds of brick and mortar.

The increase due to difference in mortar is greater for the strong New England brick than for the other kinds.

The ratio of the cube root of the dry mortar cylinder strengths (see Table 8) for the mortars of these walls is 1.38, a value within the range of variation of the wall strength ratios given in Table 13.

TABLE 12.—*Results of tests of walls with slight differences in the mortar mixtures*

[Wall type, 8-inch solid; brick, Chicago; series 2; workmanship, spread joints; curing conditions, ordinary.]

Wall Nos.	Mortar proportions (by volume)	Average wall strength	Average mortar cylinder strength	
			Wet	Dry
		Lbs./in.^{2}	*Lbs./in.*^{2}	*Lbs./in.*^{2}
160, 161, 162	1C: 3S	880	3,050	2,180
163, 164, 165	1C: 0.1L: 3S	355	3,580	2,350

TABLE 13.—*Results of tests of solid walls of series 2*

[Smooth spread mortar joints; ordinary curing conditions]

Type of wall	Kind of brick	Average wall strength		
		Cement-lime (C-L)	Cement (C)	Ratio $\frac{C}{C\text{-}L}$
		Lbs./in.²	*Lbs./in.²*	
8-inch solid	Detroit	910	1,080	1.19
	Mississippi	1,160	1,380	1.19
	New England	1,790	2,635	1.47
12-inch solid	Detroit	985	1,210	1.23
	Mississippi	1,300	1,640	1.26
	New England	1,890	2,790	1.48
4-inch economy	Mississippi	1,435	1,625	1.13
	New England	1,940	3,145	1.62

The effect of mortar on the strength of walls of different types is shown graphically in Figures 33 and 34 for the walls built of Mississippi

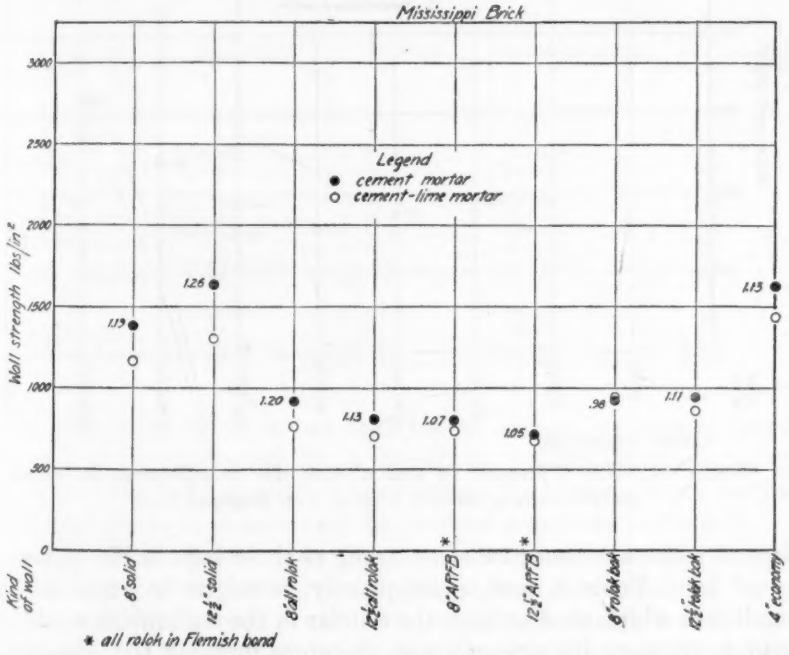

FIGURE 33.—*The differences in wall strength due to differences in mortar for the walls of series 2 built of Mississippi brick*

and New England brick, respectively. The numbers placed beside the values for the cement mortar walls are the ratios of the wall strengths of cement mortar to those of cement-lime mortar. There appears to be no definite and consistent relation for the increase in strength due to the use of cement mortar, the increase being different from the

different types of walls and usually being less for the Mississippi than for the stronger New England brick.

(E) THE EFFECT OF DAMP CURING ON THE COMPRESSIVE STRENGTH OF BRICK WALLS

One of the problems studied in this series of tests was to determine the effect of damp curing on the compressive strength of brick walls. At the time these tests were outlined there was a more or less general opinion that walls kept damp for a time after they had been built would be stronger than others allowed to age without wetting. Cylinders of Portland cement mortar (size 2 by 4 inches) aged for 60

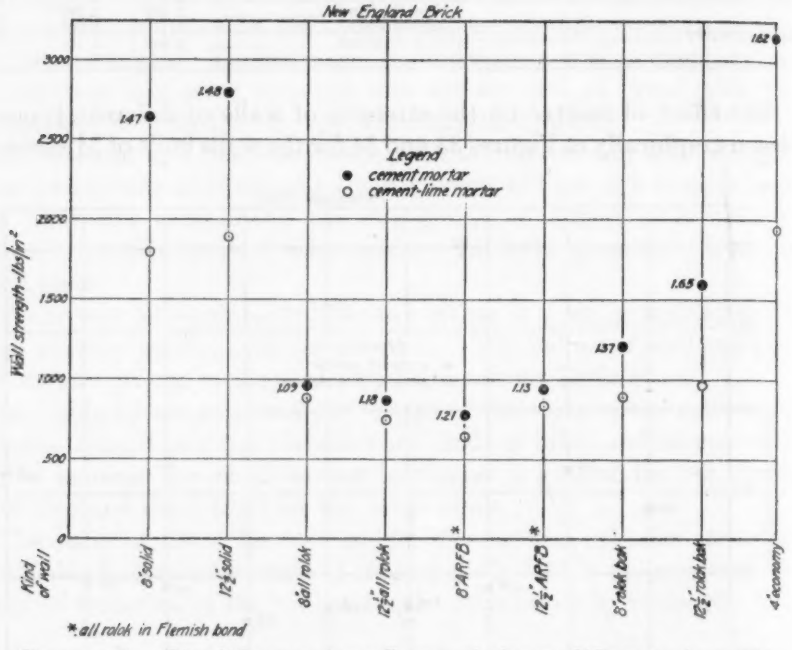

FIGURE 34.—*The differences in wall strength due to differences in mortar for the walls of series 2 built of New England brick*

days in water are about twice as strong as those kept in air, as may be noted from Table 8, and, consequently, it might be expected that conditions which tend to keep the mortar in the wall moist would also tend to increase its strength and therefore increase the strength of the wall.

Some walls of series 2, built with cement mortar, were allowed to age in the laboratory under ordinary conditions. Other similar walls listed in Tables 1 and 9 as "wetted" were covered with burlap, as shown in Figure 15. The burlap was kept damp for one week after the walls had been built and was then removed.

The results of these compressive tests of brick walls are given in Table 14.

It is seen from these data that there was no increase in the strength of the walls due to damp curing. Whether the same results would have been obtained on specimens built out of doors is, perhaps, open to question.

Although the strength of small mortar cylinders is increased by keeping them wet, there are several reasons why much greater strength in the wet walls than in the dry ones would not be expected.

In the first place, the failure in all of these walls laid in cement mortar occurred in the brick and not in the mortar. While walls similar in all respects, except as to mortar, will generally have the higher strengths with stronger mortars, the strength of the brick is probably the determining factor in wall strength when the mortars are of about the same strength.

TABLE 14.—*Effect of wetting on wall strength*

[Walls of series 2, cement mortar]

Type of wall	Kind of brick	Wall Nos.	Curing conditions	Average wall strength	Ratio of wall strengths, wetted/ ordinary
				*Lbs./in.*²	
8-inch solid	Detroit	22, 23, 24	Ordinary	1,080	
	do	33	Wetted	1,055	0.98
12-inch solid	do	28, 29, 30	Ordinary	1,210	
	do	31, 32	Wetted	1,105	.91
	Mississippi	43, 44	Ordinary	1,785	
	do	46, 47	Wetted	1,590	.89
	New England	103, 104	Ordinary	2,835	
	do	106, 107	Wetted	2,510	.89
12-inch rolok-bak	Mississippi	82, 83	Ordinary	935	
	do	85, 86	Wetted	965	1.03
	New England	142, 143	Ordinary	1,580	
	do	145, 146	Wetted	1,325	.84

In the second place, it has been found that an increase in mortar strength is accompanied by a relatively smaller increase in wall strength if the same quality of brick is used.[8] Hence, a large increase in mortar strength is necessary to produce a notable increase in wall strength. This should not, however, be taken to mean that the mortar is not a very important factor in wall strength.

It is probable, moreover, that the wetting of the walls did not increase greatly the strength of the mortar, for although the wetting would tend to retard the evaporation of moisture, the loss of moisture from the walls in dry storage proceeded at a slow rate. The moisture present in the brick and mortar at the time the walls were built evaporated at such a slow rate as to provide sufficient moisture at early ages for favorable curing conditions, since in all of these

[8] See data on wall strength and mortar strength in B. S. Tech. Paper No. 276, Compressive Strength of Sand-Lime-Brick Walls, by Whittemore and Stang.

walls the brick were probably wetter when laid than is the case in ordinary commercial practice.

Finally, a few samples of the mortar taken from these walls after test were found to contain, on the average, about 8 per cent of moisture by weight. This damp condition would tend to decrease the strength of the brick and of the mortar and, consequently, the strength of the damp cured walls. There are no definite data to show how much the strength of either the mortar or the brick was changed by the indefinite or rather nonuniform moisture content of the walls after they had aged. Numerous tests [9] have shown that Portland-cement mortars and concrete are considerably weakened when wetted just previous to testing.

The strength of some bricks is decreased by moisture. Others do not appear to have their strength influenced by this condition. Table 15 gives the compressive strengths of bricks used in this investigation when tested flatwise in the wet and dry condition, each value begin the average of 50 tests. The wet bricks had been immersed in water for 48 hours before test and were, of course, much wetter than were those in the walls at the time of test.

TABLE 15.—*Compressive strength of half brick wet and dry, flatwise*

Kind of brick	Compressive strength		Ratio wet/dry
	Wet	Dry	
	Lbs./in.²	*Lbs./in.²*	
Detroit	2,520	3,540	0.71
Mississippi	3,520	3,410	1.03
New England	6,990	8,600	.81

The values given in Table 15, purporting to show the effect of moisture on the compressive strength of brick, probably indicate a somewhat greater decrease in strength due to moisture than actually existed because of the wet plaster of Paris cap. All of the bricks were capped with plaster of Paris prior to testing and, since the strength of gypsum is greatly decreased by moisture,[10] the weakening of the caps may have affected the results.

The Detroit and New England bricks were considerably weaker when wet, while the strength of the Mississippi brick did not appear to be affected by moisture. The slightly low compressive value for these brick dry is probably due to the sampling error and not to any real difference in their compressive strengths when in different moisture conditions. Reference to Table 14, however, shows that the wet

[9] Herbert J. Gilkey, The Effect of Varied Curing Conditions Upon the Compressive Strength of Mortar and Concrete, Proc. Am. Concrete Inst., 22; 1926.

[10] W. A. Slater, Some Structural Properties of Gypsum and of Reinforced Gypsum, Trans. Ill. Acad. Sci., 9.

walls built of Detroit and New England bricks were only a little weaker relative to the companion dry walls than those built of Mississippi brick, the average ratios being 0.905 for the Detroit and New England and 0.960 for the Mississippi bricks.

Thus we have opposing effects which tend to keep the wall strength constant as between damp cured and dry walls. The dampness may tend to produce a stronger mortar, but the moisture present in the brick at the time of test weakens the wall.

It seems reasonable, then, to suppose that brick walls built with strong cement mortar and fairly wet brick will be as strong when aged in air for 60 days as they will be if they are kept damp for a short time after construction.

(b) THE EFFECT OF THE QUALITY OF WORKMANSHIP ON WALL STRENGTH

The workmanship typical of each of the two masons who built these brick walls has already been described in some detail and may be summarized as follows:

For walls of series 1, relatively high rate of laying brick, absence of mortar in the longitudinal vertical joints, and pronounced furrowing in the horizontal mortar beds; for walls of series 2, slow rate of laying brick, careful filling of the vertical joints, and smooth spread bed joints.

In Table 16 are listed those walls which show the effect of differences in workmanship. For the 8-inch solid walls of Chicago brick, the average thickness of the mortar joints was almost the same for both groups, and the 30 per cent increase in strength for the walls of series 2 must be attributed to the differences in workmanship.

The important differences as far as they could be observed consisted of the absence of furrowing of the horizontal mortar joints in series 2 and the better filling of the vertical joints. With the Mississippi brick, wall 155 of series 1 had exceptionally thick mortar joints (0.73 inch), and it may be that the greater strength of walls 37, 38, and 39, of 59 per cent, was due to their having thinner joints. The absence of furrowing and the filling of the vertical joints apparently made the 8-inch solid walls of New England brick and the 12-inch solid walls of Chicago brick of series 2 decidedly stronger than the companion walls of series 1.

The large increases in strength for the hollow walls of series 2 over the strengths of walls of series 1 was unexpected. It was supposed that the use of brick on edge in the construction of the hollow walls would not permit furrowing. However, demolition of these walls after testing showed that the mason furrowed the horizontal mortar bed on the narrow edge of the brick as consistently as on the regular solid construction. The furrow was continuous throughout the entire length of the mortar bed, but was broken up in much the same manner as were the furrows in the solid walls as shown in Figure 7.

The uneven and irregular bedding probably produced bending stresses in the bricks, which caused local concentrations of load and resulted in failure at lower loads than would have been the case with more even joints.

TABLE 16.—*Result of tests of brick walls with variations in workmanship*

[Cement mortar throughout]

Type of wall	Brick	Series 1 (furrowed joints)			Series 2 (spread joints)			Increase in wall strength, series 2 to series 1
		Wall No.	Average thickness of mortar joints	Wall strength	Wall No.	Average thickness of mortar joints	Wall strength	
			Inch	*Lbs./in.²*		*Inch*	*Lbs./in.²*	*Per cent*
8-inch solid	Chicago	13	0.56	660	160	0.57	800	
		14	.56	750	161	.59	870	
		15	.57	580	162	.55	965	
	Average		.56	665		.57	880	32
	Mississippi	155	.73	870	37	.52	1,335	
					38	.44	1,405	
					39	.40	1,405	
	Average					.45	1,380	59
	New England	154	.46	2,030	97	.36	2,040	
					98	.22	2,950	
					99	.27	2,915	
	Average					.28	2,635	30
12-inch solid	Chicago	16	.57	655	166	.49	890	
		17	.56	655	167	.51	1,080	
	Average		.56	655		.50	985	50
8-inch all-rolok	Mississippi	156	.66	440	52	.46	850	
					53	.40	735	
					54	.41	1,175	
	Average					.42	920	109
8-inch all-rolok in Flemish bond	Mississippi	157	.65	535	64	.47	825	
					65	.43	720	
					66	.43	855	
	Average					.44	800	50
8-inch rolok-bak	Mississippi	158	.62	745	76	.48	925	
					77	.42	890	
					78	.47	950	
	Average					.46	920	24

These comparisons of strengths of hollow walls lead to the belief that full spread horizontal mortar beds without furrowing are more important from a strength standpoint than the complete filling of vertical joints. In the hollow walls the longitudinal space between the rowlock wythes, of course, contained no mortar, and differences in strength were, therefore, almost entirely due to differences in the horizontal mortar beds.

The apparent effect of furrowing and unfilled vertical joints on wall strength is strikingly brought out by a comparison of the strengths of walls 155 and 159, as shown in Table 17. Both walls were built by the mason of series 1. Although wall 159, with no furrowing in the mortar beds, was built at an exceptionally fast rate, its strength was 70 per cent greater than that of wall 155 with the typical furrows.

TABLE 17.—*Effect of furrowing and unfilled vertical joints in walls of series 1*

[Type of wall, 8-inch solid; mortar, cement; brick, Mississippi]

Workmanship (type of bed joints)	Wall No.	Brick laid per hour	Average thickness of mortar joint	Wall strength
			Inch	*Lbs./in.²*
Furrowed	155	195	0.73	870
Spread, no furrowing	159	264	.62	1,480
Ratio of wall strengths				1.70

The rate of laying wall 159, as given in Tables 3 and 17, and the statement of the mason who built the walls of series 2 show that spreading the mortar bed without furrowing does not reduce the rate of laying brick. The comparative results given in Tables 16 and 17 show the remarkable increase in strength obtained by the better filling of the mortar joints. It is believed that the realization of the importance of having smooth and level horizontal mortar beds in a brick wall is the most important conclusion of these tests. This construction practice, which apparently involves no increase in labor cost, but which results in a very significant increase in strength, is strongly recommended to builders of masonry structures.

A comparison of "spread" and "shoved" workmanship for walls of series 2 is afforded in Table 18. Wall 18 of Chicago brick and "shoved" workmanship had thinner mortar joints than did the companion walls 166 and 167 built of the same kind of brick with the full spread joints of series 2. In the three groups listed in Table 18 the walls of Chicago brick constitute the only group for which the "shoved" workmanship was superior to the other. The table shows that shoved work introduces no improvement in strength over the spread and fully slushed joint workmanship which was typical of series 2.

TABLE 18.—*Comparison of "spread" with "shoved" joints for walls of series 2*

[Type of walls, 12-inch solid; mortar, cement]

Kind of brick	"Spread" joints			"Shoved" joints			Ratio of wall strength "shoved" to "spread"
	Wall No.	Average thickness of mortar joint	Wall strength	Wall No.	Average thickness of mortar joint	Wall strength	
		Inch	*Lbs./in.²*		*Inch*	*Lbs./in.²*	
Chicago	166	0.49	890	18	0.31	1,165	1.18
	167	.51	1,080				
Average		.50	985				
Mississippi	43	.51	1,710	48	.42	1,465	.89
	44	.37	1,855				
	45	.42	1,350				
Average		.43	1,640				
New England	103	.28	2,440	108	.22	2,720	.97
	104	.23	3,230				
	105	.23	2,695				
Average		.25	2,790				

Reference has been made several times to the thickness of the mortar joints as having a possible effect on wall strength. Although this investigation was not planned with a view to having thickness of mortar joint a variable for the walls, Table 3 shows that some variation did exist. A study of the data for the single walls shows that joint thickness was by no means a controlling factor in strength for the hollow walls. The thickness of the beds in the groups of solid walls of series 1 was practically uniform from wall to wall and the results of these tests throw no light on this subject.

The thickness of the mortar joints and the wall strength are given in Table 19 for 18 groups of solid walls of series 2 built with comparable workmanship and aged under ordinary conditions. The walls of each group have been arranged in the order of wall strengths, and it might be expected that the wall having the least thickness of mortar joint would have the greatest strength. In the column designated "order" of this table those groups have been classed as "regular," for which increase in joint thickness is accompanied by decreases in wall strength, as "reverse," if increase in joint thickness is accompanied by increase in wall strength, and as "irregular" for the others which follow neither of these classifications entirely.

TABLE 19.—*Effect of thickness of mortar joints on strength of solid walls of series 2*

A. CEMENT-LIME MORTAR

Type of wall	Kind of brick	Wall No.	Average thickness of mortar joint	Wall strength	Order
			Inch	*Lbs./in.²*	
8-inch solid	Detroit	19	0.39	1,060	Regular.
		20	.40	905	
		21	.44	760	
	Mississippi	36	.40	1,340	Do.
		35	.44	1,175	
		34	.56	965	
	New England	95	.28	1,875	Irregular.
		94	.35	1,785	
		96	.27	1,710	
12-inch solid	Detroit	25	.38	1,050	Do.
		27	.44	965	
		26	.38	940	
	Mississippi	40	.50	1,375	Do.
		41	.40	1,305	
		42	.44	1,225	
	New England	101	.20	1,990	Regular.
		102	.25	1,855	
		100	.33	1,815	
4-inch economy	Mississippi	90	.42	1,565	Irregular.
		88	.44	1,370	
		89	.40	1,365	
	New England	149	.30	1,975	Do.
		148	.36	1,960	
		150	.22	1,880	

TABLE 19.—*Effect of thickness of mortar joints on strength of solid walls of series 2*—Continued

B. CEMENT MORTAR

Type of wall	Kind of brick	Wall No.	Average thickness of mortar joint	Wall strength	Order
			Inch	*Lbs./in.²*	
8-inch solid	Chicago	162	0.55	965	Irregular.
		161	.59	870	
		160	.57	800	
	do	164	.57	925	Regular.
		163	.62	885	
		165	.66	755	
	Detroit	22	.38	1,305	Irregular.
		24	.43	1,050	
		23	.40	895	
	Mississippi	38	.44	1,405	Do.
		39	.40	1,405	
		37	.52	1,335	
	New England	98	.22	2,950	Regular.
		99	.27	2,915	
		97	.36	2,040	
12-inch solid	Detroit	29	.37	1,345	Do.
		28	.39	1,165	
		30	.41	1,115	
	Mississippi	44	.37	1,855	Irregular.
		43	.51	1,710	
		45	.42	1,350	
	New England	104	.23	3,230	Regular.
		105	.23	2,695	
		103	.28	2,440	
4-inch economy	Mississippi	93	.46	1,875	Reverse.
		91	.44	1,650	
		92	.41	1,350	
	New England	152	.29	3,520	Irregular.
		153	.23	3,160	
		151	.35	2,755	

If there is only a chance relation between joint thickness and wall strength, it would be expected that the "regular" and the "reverse" order would each occur three times in the 18 groups. The table shows that, of the 18 groups, 7 are regular, or two and one-third times as many as would be expected from a chance distribution. Only one reverse group is present instead of the three to be expected. The tendency is therefore for walls with thin joints to have somewhat higher strengths, although it has been impossible to find a definite relationship between these two factors.

(i) THE RELATION OF STRESS AT FIRST CRACK TO MAXIMUM STRESS

Table 20 gives the ratio of the stress at first crack to the maximum stress for the walls of series 1 with furrowed joints and for those of series 2 with full-spread joints which were cured under ordinary conditions.

For the solid walls of series 1 it appears that these ratios become greater as the strength of the mortar increases. The average ratio

for the Chicago brick walls of series 2 built with cement and cement-lime mortars is greater than for those of series 1 built with the same mortars.

The solid walls of Detroit and of New England brick, both of which had frogs, had initial signs of failure at considerably lower ratios than for the solid walls of the other kinds of brick. Whether this relatively low initial failure is due in part to the presence of the frog in these bricks and to the fact that they were more irregular in size and shape than the Chicago and Mississippi bricks is unknown.

TABLE 20.—*Relation of stress at first crack to wall strength*

[Ordinary curing conditions]

Description of groups compared	Number of walls averaged	Stress at first crack/wall strength
Series 1 (furrowed joints):		*Ratio*
Lime-mortar walls, Chicago brick	6	0.71
Cement-lime mortar walls, Chicago brick	6	.88
Cement mortar walls, Chicago brick	5	.94
All walls, Chicago brick	17	.84
Series 2 (full spread joints):		
Solid walls of Chicago brick	8	.96
Solid walls of Detroit brick	12	.64
Solid walls of Mississippi brick	18	.92
Solid walls of New England brick	18	.68
Solid walls	56	.79
All-rolok walls	24	.70
All-rolok in Flemish bond walls	24	.74
Rolok-bak walls	24	.72
Walls of Mississippi brick	54	.83
Walls of New England brick	54	.67
Walls built with cement-lime mortar	60	.72
Walls built with cement mortar	68	.73

Table 20 shows that the solid walls had a somewhat higher ratio between stress at first crack and maximum stress than the hollow walls. The ratios were about the same for the different types of hollow walls.

The walls of series 2 built with cement mortar had a higher ratio than those built with cement-lime mortar, the relative values being much the same as for walls of series 1.

It is evident from a study of Table 20 that the relation of stress at first crack to wall strength is not a constant, but varies with many of the conditions that affect wall strength.

4. WALLETTES

The results of the compressive tests of the wallettes are given in Table 21. The wallettes were built by the same mason and cured under the same conditions as the walls of the corresponding numbers. Most of the wallettes were built either on the same day as the walls or on the day after.

TABLE 21.—*Results of compressive tests of brick wallettes (gross area)*

A. WALLETTES OF SERIES 1

Type of wallette	Mortar	Kind of brick	Wallette Nos.			Average stress at first crack	Wallette strength			
			a	b	c		a	b	c	Average
						Lbs./in.²	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*
8-inch solid	Lime	Chicago	1	2	3	245	380	375	350	370
	Cement-lime	do	7	8	9	550	735	725	685	715
	Cement	do	13	14	15	665	780	885	700	790
12-inch solid	Lime	do	4	5	6	235	420	410	405	410
	Cement-lime	do	10	11	12	580	625	680	660	655
	Cement	do	16	17		690	700	810		755

B. WALLETTES OF SERIES 2

8-inch solid	Cement-lime	Detroit	19	20	21	695	1,315	705	1,120	1,045
		Mississippi	34	35	36	1,265	1,020	1,425	1,795	1,410
		New England	94	95	96	1,405	1,730	2,850	2,320	2,300
	Cement	Detroit	22	23	24	1,210	1,335	1,045	1,675	1,350
		do	33			765	865			865
		Mississippi	37	38	39	1,405	1,550	1,730	1,615	1,620
		New England	97	98	99	2,080	3,455	3,880	3,760	3,700
12-inch solid	Cement-lime	Detroit	25	26	27	865	1,265	950	845	1,020
		Mississippi	40	41	42	1,175	1,390	1,210	1,230	1,275
		New England	100	101	102	1,625	1,965	2,845	2,565	2,460
	Cement	Chicago	18			1,145	1,190			1,190
		Detroit	28	29	30	1,200	1,605	1,620	785	1,335
		do	31	32		745	1,225	1,100		1,160
		Mississippi	43	44	45	1,605	1,725	2,060	1,500	1,760
		do	46	47		1,410	1,425	2,305		1,865
		do	48			1,350	1,640			1,640
		New England	103	104	105	2,190	2,515	4,140	3,425	3,360
		do	106	107		1,950	2,355	3,790		3,075
		do	108			2,440	3,200			3,200
8-inch all-rolok	Cement-lime	Mississippi	49	50	51	510	805	845	895	850
		New England	109	110		395	1,385	2,015		1,700
	Cement	Mississippi	52	53	54	735	990	800	1,280	1,025
		New England	112	113	114	630	1,465	1,995	1,520	1,660

TABLE 21.—*Results of compressive tests of brick wallettes (gross area)*—Continued

B. WALLETTES OF SERIES 2—Continued

Type of wallette	Mortar	Kind of brick	Wallette Nos.			Average stress at first crack	Wallette strength			
			a	b	c		a	b	c	Average
						Lbs./in.²	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*
12-inch all-rolok	Cement-lime	Mississippi	55	56	57	735	720	1,115	755	865
		New England	115	116	----	715	825	1,535	----------	1,180
	Cement	Mississippi	58	59	60	695	900	820	1,030	920
		New England	118	119	----	650	1,480	1,390	----------	1,435
8-inch all-rolok in Flemish bond	Cement-lime	Mississippi	61	62	63	645	1,000	1,270	965	1,075
		New England	121	122	----	820	1,685	1,665	----------	1,675
	Cement	Mississippi	64	65	66	670	955	1,135	870	990
		New England	124	125	----	820	1,740	1,080	----------	1,410
12-inch all-rolok in Flemish bond	Cement-lime	Mississippi	67	68	69	595	875	990	1,215	1,030
		New England	127	128	----	795	1,650	1,510	----------	1,580
	Cement	Mississippi	70	71	72	760	980	1,010	1,090	1,025
		New England	130	131	----	695	1,470	1,790	----------	1,630
8-inch rolok-bak	Cement-lime	Mississippi	73	74	75	730	980	950	1,020	985
		New England	133	134	----	640	1,230	2,130	----------	1,680
	Cement	Mississippi	76	77	78	785	850	1,255	1,405	1,170
		New England	136	137	----	805	1,255	3,150	----------	2,205
12-inch rolok-bak (heavy duty)	Cement-lime	Mississippi	79	80	81	565	890	835	880	870
		New England	139	140	----	625	1,125	1,290	----------	1,205
	Cement	Mississippi	82	83	84	645	770	1,040	1,125	980
		do	85	86	----	675	775	855	----------	815
		New England	142	143	----	770	1,325	2,180	----------	1,755
		do	145	146	----	815	2,370	2,275	----------	2,320
12-inch rolok-bak (standard)	Cement	Mississippi	87	----	----	830	1,090	----------	----------	1,090

The area of the wallettes was taken as the product of the average thickness of the wallette by the minimum length. Figure 18 shows that in small specimens, with the brick clipped as little as possible, the length of the wallette may vary considerable from course to course. The values of wallette strength given in Table 21 are therefore based on minimum gross areas for the hollow as well as for the solid wallettes.

The compressive strength of the wallettes varied with the physical properties of the brick, with the type of construction, with the mortar, curing conditions, and workmanship very much as did the wall strengths.

The variation in strength from wallette to wallette in any group was much less for the specimens of series 1 than of series 2. The mason who built the specimens of series 2 did not seem to like to build the small walls and on several occasions had to be told to use as much care on them as he used on the larger specimens. The average fractional deviation of the strength values within a given group from the average was for the wallettes of series 1, 0.04, and for those of series 2 it amounted to 0.13. In drawing conclusions from the tests of series 2 it is therefore to be remembered that relatively large variations have occurred in many of the groups.

The differences in strength due to differences in the kind of brick are found only for the wallettes of series 2. All bricks for the wallettes of series 2 were soft-mud or dry-press bricks, except in the wallette 18 of Chicago brick. In all cases where groups of solid wallettes differing only in the kind of brick are compared, the New England specimens were strongest, followed in order by those of Mississippi and of Detroit brick.

As with the larger walls, the solid wallettes were stronger, based on gross area, than were any of the hollow types. The strengths based on net area were nearly the same irrespective of the type of construction for wallettes built of Mississippi brick and, while not so uniform for the wallettes of New England brick, were much more constant than for the walls previously discussed.

Table 22 shows the relative strength of the different types of walls and wallettes, the strongest being listed at the top in each group and the others in the order of their strengths. In six of the eight wall groups the types rank solid, rolok-bak, all-rolok, and all-rolok in Flemish bond, and in the two cases where this order does not hold the inversions are due to relatively small differences in strength—less than 100 lbs./in.^{2}. From the wallette tests, however, this arrangement in the order for the strengths of the different types would not be evident. In fact, only two groups of wallettes show this same order while four wallette groups rank—solid, all-rolok in Flemish bond, rolok-bak, and all-rolok. The fact that the solid wallettes were stronger than any of the hollow types shows, however, that larger strength differences are readily recognized from wallette tests.

TABLE 22.—*Relative strength of different types of walls and wallettes*

Wall thickness	Mortar	Strength rank			
		Mississippi		New England	
		Wall	Wallette	Wall	Wallette
8-inch	Cement-lime	Solid	Solid	Solid	Solid.
		Rolok-bak	A. r. F. b.	Rolok-bak	All-rolok.
		All-rolok	Rolok-bak	All-rolok	Rolok-bak.
		A. r. F. b.	All-rolok	A. r. F. b.	A. r. F. b.
	Cement	Solid	Solid	Solid	Solid.
		Rolok-bak	Rolok-bak	Rolok-bak	Rolok-bak.
		All-rolok	All-rolok	All-rolok	All-rolok.
		A. r. F. b.	A. r. F. b.	A. r. F. b.	A. r. F. b.
12-inch	Cement-lime	Solid	Solid	Solid	Solid.
		Rolok-bak	A. r. F. b.	Rolok-bak	A. r. F. b.
		All-rolok	Rolok-bak	A. r. F. b.	Rolok-bak.
		A. r. F. b.	All-rolok	All-rolok	All-rolok.
	Cement	Solid	Solid	Solid	Solid.
		Rolok-bak	A. r. F. b.	Rolok-bak	Rolok-bak.
		All-rolok	Rolok-bak	A. r. F. b.	A. r. F. b.
		A. r. F. b.	All-rolok	All-rolok	All-rolok.

A. r. F. b.=all rolok in Flemish bond.

For the solid wallettes the results given in Table 21 show that the mortar had about the same effect on wallette strength as on wall strength. The lime-mortar specimens were weakest and the cement-mortar specimens strongest for all groups of solid wallettes which differed only in the mortar mixtures used.

Keeping the wallettes damp for seven days after construction did not make them stronger than similar specimens cured under ordinary conditions except for the group for 12-inch rolok-bak wallettes of New England brick (Table 23). Specimens 142 and 143, cured under ordinary conditions, had an average strength of 1,755 lbs./in.^{2}, while the similar wallettes, 145 and 146, which were damp cured, had a strength of 2,320 lbs./in.^{2}. In the other five comparable groups the ratio of wallette strengths, damp cured to ordinary, ranged from 0.64 for the 8-inch solid wallettes of Detroit brick to 0.99 for the 12-inch solid specimens of Mississippi brick.

TABLE 23.—*Effect of wetting on wallette strength*

[Wallettes of series 2, cement mortar]

Type of wallette	Kind of brick	Wallette Nos.	Curing conditions	Average wallette strength	Ratio of wallette strengths wetted/ ordinary
				Lbs./in.^{2}	
8-inch solid	Detroit	22, 23, 24	Ordinary	1,350	0.64
		33	Wetted	865	
12-inch solid	do	28, 29, 30	Ordinary	1,335	.87
		31, 32	Wetted	1,165	
	Mississippi	43, 44	Ordinary	1,890	.99
		46, 47	Wetted	1,865	
	New England	103, 104	Ordinary	3,330	.92
		106, 107	Wetted	3,075	
12-inch rolok-bak (heavy-duty)	Mississippi	82, 83	Ordinary	905	.90
		85, 86	Wetted	815	
	New England	142, 143	Ordinary	1,755	
		145, 146	Wetted	2,320	1.32

The only comparison due to difference in the workmanship is between wallette 18 of series 2 built with shoved workmanship and wallettes 16 and 17 of series 1 with the typical furrowed joint workmanship of this series. The relative strengths are as 1,190 is to 755, giving an increase in strength with shoved joints of 58 per cent over that obtained with furrowed joints.

A study of the relation between stress at first crack and wallette strength shows that the same conclusions may be drawn as from the wall tests. The main difference between the wall and wallette results is that the hollow wallettes had considerably lower ratio of stress at first crack to final strength than was found from the wall tests.

The lowering of the ratio for strength at first crack to ultimate strength of hollow wallettes is brought about not by the strength at first crack being low, but by the ultimate strength being high as compared with the corresponding hollow walls. The difference in behavior of hollow walls and wallettes is apparently explainable by considering the relative slenderness ratios of the withes when the connecting headers are broken. For hollow walls (all-rolok or all-rolok in Flemish bond) when the headers are broken, there results two unsupported sections 9 feet high by 2¼ inches thick. Through column action these collapse. The wallettes, however, give sections 34 inches by 2¼ inches. This gives a slenderness ratio so low that column action does not take place and the load increases to the point where crushing of the brick results. The values for slenderness ratios (l/r) for wall and wallette sections (108 inches by 2¼ inches and 34 inches by 2¼ inches) are 166 and 52.4, respectively.

Table 24 gives average values of the ratio of wall strength to wallette strength. These values show that the ratio (for the solid specimens for series 2) becomes less as stronger brick are used. In other words, the use of strong brick gives a greater increase in wallette strength than in wall strength.

In Figure 35 are plotted the solid wall strengths against the solid wallette strengths for each group in both series for which direct comparisons can be made. The average ratio from Table 24, represented by the diagonal line in the figure, of the wall strength to the wallette strength is 0.86, but the plotted points indicate the trend toward proportionately greater wallette strength for the stronger specimens. The ratio for the solid and rolok-bak specimens is greater than for those types in which all the withes are laid on edge.

The average values of the ratio of wall strength to wallette strength are about the same when the specimens are laid in cement-lime mortar as in cement mortar.

TABLE 24.—*Relation of wall to wallette strengths*

Description of groups compared	Wall strength / Wallette strength
	Ratio
Average for all solid specimens of both series	0.86
Series 2:	
Solid specimens of Detroit brick	.93
Solid specimens of Mississippi brick	.90
Solid specimens of New England brick	.79
Solid specimens	.87
All-rolok specimens	.75
All-rolok in Flemish bond specimens	.63
Rolok-bak specimens	.86
Specimens laid in cement-lime mortar	.78
Specimens laid in cement mortar	.81

In general, then, it may be stated that solid wallette strengths are affected by differences in brick, mortar, curing conditions, and work-

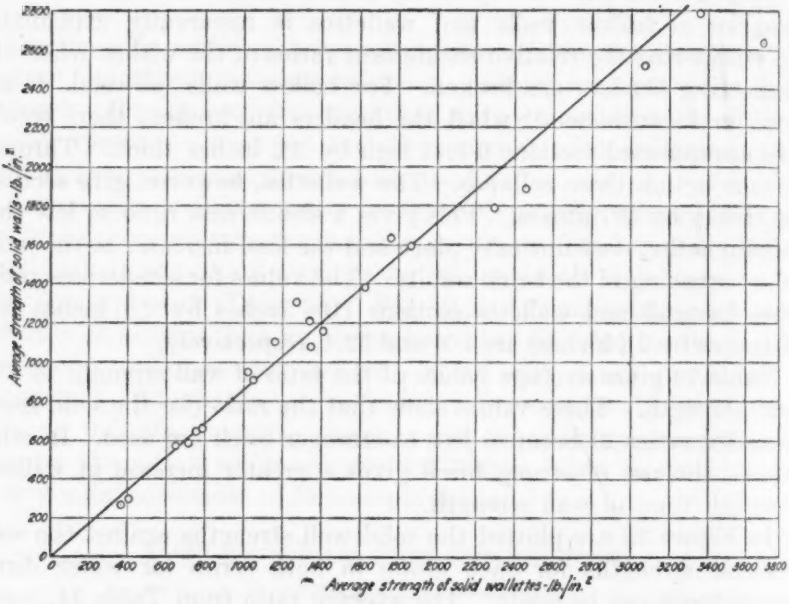

FIGURE 35.—*Relation of wall to wallette strengths for solid specimens*

manship in very much the same way as are solid wall strengths. In fact, the general tendencies of strength changes for the hollow specimens are also indicated by wallette strengths. For the hollow specimens the relation between the strengths of the wallettes and the walls is not as well defined, but the wallette strengths may serve as a measure of the strengths of both types of walls.

5. RELATIONS BETWEEN THE STRENGTHS OF THE WALLS AND THE STRENGTHS OF THE BRICKS AND WALLETTES

The object of the tests of these brick walls was to find, if possible, some strength property of the bricks or of smaller walls which will be a measure of the strength of the solid walls. The ratios of the compressive strengths of the walls to the various properties of the bricks and to the compressive strengths of the wallettes are given in Table 25. This table is divided into seven groups, in each group of which the variable is the kind of brick. The ratio of wall strength to brick or wallette strength, of course, varies from group to group because of differences in mortar or in workmanship, but in any one group that ratio is the best measure of wall strength which is most nearly constant for the different kinds of bricks. A measure of the constancy of this ratio is given by dividing the mean deviation of the separate ratios by the mean of the ratios in a group. The smaller this value is the better this property of the brick serves as a measure of wall strength. Actually the magnitudes of the deviations of these ratios from their mean are measures of the degree to which the values for wall strength deviate from a linear relation with the particular brick strength to which they refer. If a much wider range in brick strengths had been involved, it is possible that the determination of the properties of brick which were the most consistent measures of wall strength should be based upon the consistency of the data with respect to a more general form of relationship that might not necessarily be linear.

TABLE 25.—*Relation of wall strength to strength of bricks and wallettes*

Group	Kind of brick	Wall Nos.	Number of walls in average	Average wall strength[1]	Ratios and their deviations of the compressive strengths of the walls to—											
					Compressive strength of half bricks flatwise[2]		Compressive strength of half bricks edgewise[2]		Modulus of rupture of bricks flatwise[2]		Tensile strength of bricks[2]		Shearing strength of bricks[2]		Compressive strength of wallettes[3]	
					Ratio	Mean deviation/mean	Ratio	Mean deviation/mean	Ratio	Mean deviation/mean	Ratio	Mean deviation/mean	Ratio	Mean deviation/mean	Ratio	Mean deviation/mean
				Lbs./in.[2]												
A. 8 and 12 inch solid walls of series 1, lime mortar.	Chicago	1 to 6	6	287	0.088	0.09	0.086	0.10	0.23	0.40	0.69	0.35	0.26	0.02	0.74	0.01
	Sand-lime	1 to 6	6	302	.073		.109		.54		1.44		.25		.72	
B. 8 and 12 inch solid walls of series 1, cement-lime mortar.	Chicago	7 to 12	6	587	.18	.09	.18	.10	.48	.40	1.4	.36	.53	.02	.86	.10
	Sand-lime	7 to 12	6	622	.15		.22		1.11		3.0		.51		.71	
C. 8 and 12 inch solid walls of series 2, cement-lime mortar.	Detroit	19 to 21 and 25 to 27	6	945	.27		.29		1.4		4.3		.81		.92	
	Mississippi	34 to 36 and 40 to 42	6	1,230	.36	.18	.34	.27	1.5	.07	3.9	.12	.77	.17	.92	.08
	New England	94 to 96 and 100 to 102	6	1,840	.21		.16		1.2		3.1		.52		.77	
D. 4-inch solid walls of series 2, cement-lime mortar.	Mississippi	88 to 90	3	1,430	.42	.29	.39	.39	1.7	.13	4.5	.17	.90	.24	------	-------
	New England	148 to 150	3	1,940	.23		.17		1.3		3.2		.55		------	
E. 8 and 12 inch solid walls of series 1, cement mortar.	Chicago	13 to 17	5	660	.20		.20		.54		1.6		.60		.85	
	Mississippi	155	1	870	.26	.09	.24	.20	1.06	.29	2.7	.28	.55	.10	------	.06
	New England	154	1	2,030	.24		.18		1.31		3.4		.57		------	
	Sand-lime	13 to 18	6	905	.22		.33		1.62		4.3		.74		.76	
F. 8 and 12 inch solid walls of series 2, cement mortar.	Chicago	160 to 167	8	897	.27		.27		.73		2.2		.82		------	
	Detroit	22 to 24 and 28 to 30	6	1,145	.32	.15	.35	.20	1.71	.26	5.2	.24	.98	.10	.85	.05
	Mississippi	37 to 39 and 43 to 45	6	1,510	.44		.42		1.84		4.8		.95		.89	
	New England	97 to 99 and 103 to 105	6	2,710	.32		.24		1.75		4.5		.76		.77	
G. 4-inch solid walls of series 2, cement mortar.	Mississippi	91 to 93	3	1,625	.48	.14	.45	.25	2.0	0.00	5.1	.01	1.02	.07	------	-------
	New England	151 to 153	3	3,145	.37		.27		2.0		5.2		.89		------	
Weighted average					------	.14	------	.22	------	.22	------	.22	------	.11	------	.06

[1] Averaged from values given in Table 9 of this paper for all but the sand-lime brick. The values for sand-lime brick are given in Table 5, p. 65, Technologic Paper No. 276.
[2] Averaged from values given in Table 6 of this paper for all but the sand-lime brick. The values for sand-lime brick are given in Table 3, p. 62, Technologic Paper No. 276.
[3] Averaged from values given in Table 21 of this paper for all but the sand-lime brick. The values for sand-lime brick are given in Table 7, p. 70, Technologic Paper No. 276.

For the range in strengths found in these tests, however, it is believed that the basis of comparison used does not involve errors sufficiently large to affect the conclusions stated.

The walls of series 1, which were built of Chicago brick, are directly comparable to the sand-lime brick walls (see footnote 6, p. 518) which had previously been tested at the Bureau of Standards. These comparisons are given in groups A, B, and E for the different mortars. The ratios for compressive strength of half brick flatwise, shearing strength, and wallette strength are more constant than for the other brick strength ratios.[11]

In groups C, D, and G, where the bricks are all molded, the ratio of wall strength to modulus of rupture flatwise is the most constant of all the brick-strength ratios, and this would also be true for groups E and F if the end-cut Chicago bricks were excluded.

For the latter, the transverse strength is high in comparison with the compressive strength (Table 7), and with this brick the wall strength was quite apparently determined more by the compressive strength than the other.

The weighted averages of the mean deviations divided by the mean, calculated by giving the value for each group a weight proportional to the number of ratios in that group, are also given in Table 25 for the different ratios. A comparison of these weighted average values shows that the shearing strength appears to be the best brick-strength property for predicting the strength of the wall. It must be pointed out, however, that the values given in Table 6 for shearing strength represent only a small number of samples as compared to the other brick-strength values and that the shearing tests were made on specimens which differed in thickness.

The compressive strength of the half brick flatwise is the next best measure of wall strength after the shearing strength, for its mean deviation divided by mean of 0.14 is considerably less than for the compressive strength edgewise, modulus of rupture, or tensile strength.

On the average, however, the compressive strength of the wallettes is by far the most consistent value for determining wall strengths.

[11] In the paper by J. W. McBurney entitled "The Effect of Strength of Brick on Compressive Strength of Brick Masonry," Proc. Am. Soc. Testing Materials, 28, Pt. II, p. 605, 1928, somewhat similar comparisons were made, but the conclusion was drawn that the compressive strength (flatwise) of the bricks was the most consistent measure of the strength of the walls. Because of an error in calculations, which was discovered after that paper had been published, the values given for the shearing strengths for all bricks except the sand-lime were double the true values, and for this reason, the strengths of the bricks in shear was not found to be closely related to the strength of the walls. The values given in McBurney's paper for the other strength properties of the bricks differ slightly in some cases from those given in the present paper. This, however, is due to the fact that, in the previous paper, a study was made of methods of sampling and some of the values given were the averages of more than one sample, whereas those given in the present paper are the results of tests of samples selected specifically for the investigation reported herein. Had there been no error in the data on the shearing strength of the bricks, there would have been no essential difference in the numerical data of the two reports.

The mean deviation divided by the mean value is consistently low for each of the five groups as well as having a weighted average value of only about half that of the best brick-strength property.

A large number of testing machines are now available in the United States which may be used for wallette tests. The tests of wallettes built of the brick to be used and laid in the mortar mixture specified can confidently be expected to give strength values which will seldom exceed the strength of a large wall by as much as 25 per cent. The prediction of wall strength from any brick strength value appears to be very uncertain because of differences in the method of manufacture of the brick and because different factors must be used for different mortars and workmanships.

Table 26 gives the relation between wall stress at first crack and the various strength properties of the bricks and to the strength of the wallettes. The weighted average values of mean deviation to mean show that the wallette strength is a better measure of wall stress at first crack than are any of the brick strengths. Of the brick strengths the shearing strength was the most consistent measure and there was no important difference in the consistencies obtained for the other strength properties.

TABLE 26.—*Relation of wall stress at first crack to strength of bricks and wallettes*

Group	Kind of brick	Wall Nos.	Number of walls in average	Average wall stress at first crack [1]	Ratios and their deviations of the wall stress at first crack to—											
					Compressive strength of half bricks, flatwise [2]		Compressive strength of half bricks, edgewise [2]		Modulus of rupture of bricks, flatwise [2]		Tensile strength of bricks [2]		Shearing strength of bricks [2]		Compressive strength of wallettes [3]	
					Ratio	Mean deviation/mean	Ratio	Mean deviation/mean	Ratio	Mean deviation/mean	Ratio	Mean deviation/mean	Ratio	Mean deviation/mean	Ratio	Mean deviation/mean
				Lbs./in.²												
A. 8 and 12 inch solid walls of series 1, lime mortar.	Chicago	1 to 6	6	205	0.062	0.11	0.61	0.10	0.17	0.37	0.49	0.34	0.19	0.06	0.53	0.03
	Sand-lime	1 to 6	6	208	.050		.75		.37		.99		.17		.50	
B. 8 and 12 inch solid walls of series 1, cement-lime mortar.	Chicago	7 to 12	6	515	.16	.14	.15	.09	.42	.37	1.2	.33	.47	.07	.75	.10
	Sand-lime	7 to 11	5	510	.12		.18		.91		2.4		.41		.61	
C. 8 and 12 inch solid walls of series 2, cement-lime mortar.	Detroit	19 to 21 and 25 to 27	6	553	.16	.40	.17	.41	.83	.29	2.5	.22	.47	.28	.54	.24
	Mississippi	34 to 36 and 40 to 42	6	1,140	.33		.31		1.39		3.6		.72		.85	
	New England	94 to 96 and 100 to 102	6	1,134	.13		.10		.73		1.9		.32		.48	
D. 4-inch solid walls of series 2, cement-lime mortar.	Mississippi	88 to 90	3	1,373	.40	.48	.38	.55	1.68	.35	4.3	.34	.86	.42	------	--------
	New England	148 to 150	3	1,233	.14		.11		.80		2.1		.35		------	
E. 8 and 12 inch solid walls of series 1, cement mortar.	Chicago	13 to 17	5	624	.19	.16	.19	.21	.51	.23	1.5	.20	.57	.10	.80	.15
	Mississippi	155	1	870	.26		.24		1.06		2.7		.55		------	
	New England	154	1	1,500	.17		.13		.97		2.5		.42		------	
	Sand-lime	13 to 18	6	700	.17		.25		1.25		3.3		.57		.59	
F. 8 and 12 inch solid walls of series 2, cement mortar.	Chicago	160 to 167	8	856	.26	.21	.26	.19	.70	.22	2.1	.18	.78	.13	------	.14
	Detroit	22 to 24 and 28 to 30	6	795	.22		.24		1.19		3.6		.68		.59	
	Mississippi	37 to 39 and 43 to 45	6	1,330	.39		.37		1.62		4.2		.84		.78	
	New England	97 to 99 and 103 to 105	6	2,028	.24		.18		1.31		3.4		.57		.57	
G. 4-inch solid walls of series 2, cement mortar.	Mississippi	91 to 93	3	1,575	.46	.28	.43	.37	1.9	.12	5.0	.14	.99	.21	------	--------
	New England	151 to 153	3	2,274	.26		.20		1.5		3.8		.64		------	
Weighted average					------	.25	------	.27	------	.27	------	.24	------	.17	------	.14

[1] Averaged from values given in Table 9 of this paper for all but the sand-lime brick. The values for sand-lime brick are given in Table 5, p. 65, Technologic Paper No. 276.
[2] Averaged from values given in Table 6 of this paper for all but the sand-lime brick. The values for sand-lime brick are given in Table 3, p. 62, Technologic Paper No. 276.
[3] Averaged from values given in Table 21 of this paper for all but the sand-lime brick. The values for sand-lime brick are given in Table 7, p. 70, Technologic Paper No. 276.

V. CONCLUSIONS

The results of these compressive tests of 168 walls and of 129 wallettes, built of 4 kinds of common brick laid in 3 mortar mixtures, with 10 types of wall construction, with differences in workmanship and in curing conditions lead to the following conclusions:

1. The average strengths of solid walls built of end-cut Chicago brick (average compressive strength of half bricks flatwise, 3,280 lbs./in.^{2}) were as follows:

Lime mortar walls, 287 lbs./in.^{2}.
Cement-lime mortar walls, 587 lbs./in.^{2}.
Cement mortar walls, 661 lbs./in.^{2}.

A contract for building these walls was let, on a lump-sum basis, to a brick mason who specialized in small contracts. The work was done without supervision and was characterized by absence of mortar in the longitudinal vertical joints and deep furrowing of the horizontal beds.

2. With carefully supervised workmanship, the average strengths of solid walls, which were built by another mason hired by the day without regard to output and which had completely filled vertical joints and smooth spread horizontal mortar beds, were as follows:

Kind of brick	Compressive strength of half brick, flatwise	Average compressive strength of solid walls	
		Cement-lime mortar	Cement mortar
	Lbs./in.^{2}	*Lbs./in.*^{2}	*Lbs./in.*^{2}
Chicago	3,280	----------	805
Detroit	3,540	945	1,145
Mississippi	3,410	1,300	1,550
New England	8,600	1,875	2,855

3. The strengths of the solid walls were more closely related to the shearing strength of the bricks than to any other strength property measured. The compressive strength of the half bricks flatwise appeared to be the next best measure and was better than the compressive strength on edge, the modulus of rupture, or the tensile strength of the bricks.

4. On the average, the compressive strength of the wallettes was by far a more consistent measure of the strength of the walls than any of the brick strength values. In predicting wall strengths from brick strengths, effects of mortar and workmanship must be taken into account, while from wallette strengths only a single value need be determined. These tests show that the average strength of the walls was from about 60 to 90 per cent of the average wallette strength.

5. The strength of the solid walls, which were built by contract, varied about as the cube root of the compressive strength of the mortar cylinders (2 inches in diameter and 4 inches long) which were made

from the mortar of the walls and cured under the same conditions. For the solid walls, built under careful supervision, the increase in strength for cement-mortar walls over those laid in cement-lime mortar was about 20 per cent for walls of Detroit and Mississippi brick and about 50 per cent for walls of New England brick, while the average ratio of the cube roots of the mortar cylinder strengths (cement and cement-lime mortars) was 1.38.

6. With brick the cross sections of which closely approximated rectangles the strengths of the hollow walls varied about as the net areas in compression. When the brick were warped, the strength of the hollow walls was found to be less than that expected from the net area.

7. Construction data show that there is a saving in materials and in time for hollow walls of brick as compared with solid walls.

8. The condition of the horizontal mortar beds in the walls affected the wall strength. Walls in which the beds were smooth were stronger than walls in which the mortar beds were furrowed by from 24 to 109 per cent.

9. Walls laid in cement mortar and kept damp for seven days after construction were not stronger at the age of 60 days than similar walls cured in the laboratory under ordinary conditions.

10. The results of the wallette tests, in which the same variables occurred as in the larger walls, lead in general to the conclusions deduced from the wall tests.

VI. APPENDIX

1. REPORTS ON WORKMANSHIP

It will be observed that no opinions have been offered in the paper as to the grading or classification of the two types of workmanship used. It was made a regular procedure to ask the opinions of such architects, engineers, and contractors who visited the bureau during the progress of this work as to their grading of the workmanship. The opinions expressed were quite variable. The only conclusion warranted was that the workmanship used in different parts of the country varied.

However, in the original program for these tests provision was made for inspection by three different bodies—the American Institute of Architects, the Supervising Architect's Office of the Treasury Department, and the International Bricklayers, Masons and Plasterers' Union.

The American Institute of Architects designated A. L. Harris, municipal architect for the District of Columbia. J. W. Ginder represented the Supervising Architect's Office. No report was received from the International Bricklayers, Masons and Plasterers' Union.

Their reports, in so far as they deal with workmanship, are here reproduced.

(a) COMMENTS BY J. W. GINDER

The physical characteristics of the units employed, the mortar mixtures, the strengths developed, and the technical deductions having been fully covered by others, the following comments are intended to bear only upon the practical aspect of the investigation.

Considering first the manner in which the test units were constructed: Series No. 1 was performed under contract with a mason who also performed the work, so that his every incentive both as a contractor and workman was to complete the work in as short a time as was consistent with obtaining acceptable results. The work was without supervision, except as understood in the preparation of mortar and in the laying up of one wall, so that the mason was free to adopt those methods which appeared to best serve his own interests.

This, it is understood, was one of the purposes of this line of procedure. The resulting work was characterized, as shown by subsequent tests, by furrowing of the mortar beds, the almost complete absence of mortar in the vertical longitudinal joints, and only such mortar in the end joints as was forced in by the "shoving" process of bedding and by depositing the subsequent mortar bed.

All circumstances considered, I believe that this very closely approximates the quality of work generally obtained in commercial construction, where close supervision is not to be expected and the most cogent consideration is economy.

Series No. 2, being built by day labor, exactly the opposite incentive was provided, and it was to the interest of the mason to work deliberately and to prolong the job, in addition to which, it is understood that he was instructed, except in certain instances, to eliminate shoving, that furrowing the beds was prohibited, and that he was to use his best workmanship.

Under these instructions he carefully leveled the beds and slushed all joints full. The subsequent tests showed the wall sections laid up by him to be without voids, and in every way, so far as workmanship was concerned, to be of the highest type for common brickwork.

I believe that such work as of the type which could be expected only under a definite specification, followed by careful supervision, such as would obtain for a high-class public or private structure, where considerations of cost were more or less subordinate.

It should be noted, however, that neither mason was under any restriction as to the thickness of bed to be maintained. I believe that if such a restriction had been imposed, say to a half inch or under, that much of the work performed under series No. 1 might have been of better character with regard to bedding, in that "tapping home" the brick to a reasonably narrow point would have tended to more completely eliminate the furrow in the bed.

As to the curing of the walls, it is noted that no increase in strength was found as a result of damp curing where this was employed, in contrast with those units which were cured in the laboratory under ordinary conditions.

I believe that owing to the saturation of the brick prior to laying and the subsequent protection of the walls from the direct heat of the sun, that all walls were in reality damp cured, the difference being one of degree only, and that if the damp-cured walls were placed in comparison with others laid up under ordinary conditions of outside exposure, a difference in favor of the damp curing might be found.

This theory would seem to be supported to some extent at least by the demonstrated increase in strength of damp-cured mortars over others not so treated.

(b) COMMENTS BY A. L. HARRIS

The walls were laid up in different kinds of mortar and erected by two different mechanics, one of whom laid the bricks to conform with the highest standards of bricklaying, the other laying the bricks according to ordinary every-day methods common to investment building and ordinary commercial work.

The brickwork done by the first mechanic was characterized by deep scoring of the mortar bed with the trowel, buttering a portion of the header only, and the omission of mortar in the center of the walls, except that which is forced into the joints by bedding the brick in the mortar. This gave a very porous or cellular construction to the interior of the wall and was comparable to the kind of brickwork found in ordinary investment and commercial work.

The brickwork done by the second mechanic was characterized by smooth, level bed joints, buttering the entire end of the header and slushing full all vertical interior joints, making a job comparable with what is known as "solid construction."

The class of workmanship in the walls built by the second mechanic (series 2) compares favorably with that obtained by the District of Columbia in its building contracts. The specifications prepared in the municipal architect's office call for all brickwork to be executed with hard-burned red bricks laid in 1 to 3 Portland cement mortar, to which is added hydrated lime not to exceed 15 per cent of the volume of the cement. The brickwork is laid solid throughout, slushing all joints full. The bricks in the interior of the wall are shoved up in a full bed of mortar. This work is inspected by a superintendent of construction, who is constantly on the job during working hours.

WASHINGTON, May 11, 1928.

DETERMINATION OF MANGANESE IN STEEL AND IRON BY THE PERSULPHATE-ARSENITE METHOD

By H. A. Bright and C. P. Larrabee

ABSTRACT

The advantage of using phosphoric acid in the persulphate-arsenite method and the effect of certain dissolved salts on the titration of permanganic acid by sodium arsenite are discussed. A description is given of the persulphate-arsenite method as used at the Bureau of Standards. In the recommended procedure, which embodies no new principles, as much as 20 mg of manganese can be handled. It is therefore possible to use 1 g samples in practically all cases. The results obtained by this procedure are much better than those obtained on smaller samples by the ordinary persulphate method and are practically of the same order of accuracy as obtained by the standard and much more elaborate bismuthate method.

CONTENTS

	Page
I. Introduction	573
II. Historical	574
III. Experimental	574
IV. Recommended procedure	577

I. INTRODUCTION

In the persulphate-arsenite method for the determination of manganese in iron and steel manganese is converted to permanganic acid by oxidation with ammonium persulphate in a dilute nitric acid solution containing a small amount of a dissolved silver salt. The permanganic acid is titrated with a standard solution of sodium arsenite. Determinations can be quickly made and, hence, the method is extensively used in steelworks laboratories. Most of the procedures used are essentially the same as the one described in the American Society for Testing Materials Standards.[1] However, the method is subject to certain limitations: That is (1) the use of a small sample and (2) difficulty in always obtaining proper oxidation of the manganese. The work discussed herein was done for the purpose of securing data whereby the method might be improved.

[1] A. S. T. M. Standards, 1927, Pt. I, p. 287.

II. HISTORICAL

The oxidation of Mn^{II} to Mn^{VII} by ammonium persulphate with silver nitrate as a catalyst was first described by Marshall.[2] Walters[3] applied the method to the oxidation of manganese in steels and estimated the permanganic acid by a colorimetric method. E. Proctor Smith[4] oxidized manganese in the same way and titrated the permanganic acid with a solution of sodium arsenite. A number of modifications of Smith's procedure have been published from time to time. In applying the persulphate-arsenite method to manganese in tungsten steels Nicolardot and Levi[5] used a mixture of sulphuric, nitric, and phosphoric acids. The phosphoric acid was used to keep the tungsten in solution. Ward[6] likewise treated tungsten steels with dilute sulphuric acid, then added nitric and phosphoric acids, and boiled until tungsten carbides dissolved. Mathevet[7] also published a procedure in which a mixture of the three acids was used to dissolve a 1 g sample of steel. He stated that the presence of phosphoric acid during oxidation prevents the precipitation of manganese dioxide which always occurs in nitric acid solution when the amount of manganese exceeds 8 to 10 mg. Willard and Greathouse[8] found that phosphoric acid is efficient in preventing the precipitation of manganese compounds during oxidation with periodate. Eder,[9] Bertiaux,[10] Travers,[11] and Mukerjee[12] used phosphoric acid in connection with the determination of manganese by the persulphate method. Travers, by the aid of metaphosphoric acid (HPO_3), quantitatively oxidized 0.50 g of Mn^{II} to Mn^{VII}, but he used hydrogen peroxide to titrate the permanganate because, as indicated later, the arsenite end point is not satisfactory for amounts of manganese above 20 mg. Kelley et al.[13] and Hall and Carlson[14] employed the potentiometric method for the titration of permanganic acid. The former used mercurous nitrate and the latter sodium arsenite.

III. EXPERIMENTAL

The ordinary persulphate-arsenite method is not suited to the determination of more than 2 to 3 mg of manganese. Furthermore, the amounts of reacting constituents can not be modified to take care of more than approximately 7 mg of manganese. As previously pointed out, larger amounts of manganese can be handled when phosphoric acid is employed. All of the experiments were, therefore, made with acid mixtures containing phosphoric acid.

[2] Chem. News, **83**, p. 76; 1901.
[3] Chem. News, **84**, p. 239; 1901.
[4] Chem. News, **90**, p. 237; 1904.
[5] Rev. Métal, **16**, p. 201; 1919.
[6] Chem. and Met., Eng. **23**, p. 28; 1920.
[7] Ann. anal. chim. appl., **5**, pp. 99–108; 1923.
[8] J. Am. Chem. Soc., **39**, p. 2366; 1917.
[9] Chem. Zeit., **46**, No. 144, p. 1085; 1922.
[10] Bull. soc. chim. de France, **35**, p. 1335; 1925.
[11] Ann. chim., **6**, p. 56; 1926.
[12] Analyst, **52**, p. 689; 1927.
[13] J. Ind. Eng. Chem., **10**, p. 22; 1918.
[14] J. Am. Chem. Soc., **45**, p. 1615; 1923.

Bertiaux has shown that with phosphoric acid present 100 mg of manganese per 200 to 225 ml can be oxidized to permanganic acid by persulphate and a silver nitrate catalyst without any separation of manganese dioxide. He titrated the permanganic acid with ferrous sulphate or oxalic acid because the theoretical factor which he used for the arsenite solution did not hold for manganese in excess of 4 mg. These first two reducing agents, however, react with chromates and can not be used for general steelwork. It is therefore more desirable to use arsenite even though the amount of manganese must be limited. The end point with arsenite can be observed fairly well with 20 mg of manganese, but it is best not to use more than 15 mg for accurate analyses.

The observations incident to the experimental work on the acidity, concentration of reagents, etc., presented in a summarized form, are as follows:

In solutions containing 10 mg of manganese per 100 ml manganese dioxide is precipitated during oxidation if 0.01 g of silver is used. Oxidation is quantitative with 0.02 to 0.03 g of silver. The use of 0.05 g of silver (0.079 g of silver nitrate) insures an ample margin of safety.

With this amount of silver nitrate and 1.5 g of ammonium persulphate, some manganese dioxide is precipitated. With 2.5 g of persulphate, oxidation of the manganese is satisfactory.

One milliliter of phosphoric acid gives satisfactory conditions for the oxidation of 12 mg of manganese in the presence of 1 g of iron, but it is necessary to use 3 to 4 ml of phosphoric acid in order to avoid the color interference of ferric iron.

The amounts of nitric and sulphuric acids can be varied somewhat without affecting the results, provided the arsenite is standardized by titrating in solutions containing the same concentration of acids.

The time required to quantitatively oxidize the manganese to permanganic acid depends upon the temperature, other conditions being constant. It was observed that oxidation is complete if the persulphate is added to a cool solution which is rapidly brought to boiling temperature and boiled about a half minute.

Addition of sodium chloride, after the manganese has been oxidized, to remove the silver ion is recommended in a number of methods, for it prevents reoxidation of manganese by the residual persulphate during the titration with arsenite in the hot solutions that are used by some analysts. The end point of the titration is affected by the amount of chloride used,[15] and for accurate work the amounts of sodium chloride and silver nitrate must be held within very narrow limits. If the titration is carried out at temperatures below 25° C.,

[15] Also noted by Hall and Carlson, J. Ind. Eng. Chem., **10**, p. 22; 1918.

sodium chloride is not needed, for no appreciable reoxidation by persulphate takes place in the time necessary for titration.

As a result of numerous tests it was noted that the end point taken when permanganic acid is titrated with sodium arsenite is slightly influenced by the silver salt, the persulphate, and the degree of acidity.[16] An acid solution of permanganic acid when titrated with sodium arsenite does not react in accordance with the ratio Mn_2O_7: 2MnO, but more nearly as indicated by the ratio Mn_2O_7:Mn_3O_5. In the presence of the silver ion the reduction of permanganate by arsenite is significantly less than when silver is absent. It was observed, however, that solutions of permanganic acid in which the concentrations of silver, acid, and persulphate were kept constant could be titrated with arsenite to reproducible end points. It seems possible, therefore, that the arsenite solution might be standardized with a permanganate solution, the titer of which had been determined by means of a primary standard such as sodium oxalate. It is general practice in standardizing the arsenite solutions to use a steel in which the manganese has been determined by some other method. This, of course, introduces into the persulphate-arsenite method those errors incident to the evaluation of the manganese in the standard steel.

The most desirable conditions for the standardization of the arsenite solution were established by the following experiments. In the first series 20 ml of 0.03 *N* potassium permanganate was added to the solution of the reagents, prepared according to the recommended method (described later), and titrated directly with arsenite. In a second series the same amount of potassium permanganate was reduced with sulphurous acid, then oxidized according to the recommended method and titrated with arsenite. The third series was the same as the first except that 1 g of electrolytic iron (manganese 0.002 per cent) was present in the acid solution. The results are shown in Table 1.

TABLE 1.—*Results obtained by standardization of the arsenite solution with standard potassium permanganate*

	0.03 *N* $KMnO_4$	Arsenite solution
	ml	*ml*
(1) $KMnO_4$, direct titration	20.00	16.46
	20.00	16.47
	20.00	16.46
(2) $KMnO_4$, reduced and oxidized	20.00	16.45
	20.00	16.44
	20.00	16.46
(3) Same as (1) but 1 g of electrolytic iron present	20.00	[a] 16.46
	20.00	[a] 16.43
	20.00	[a] 16.47

[a] 0.05 ml has been subtracted for the manganese in the electrolytic iron.

[16] This has also been noted by Geloso, who states in Compt. rend., **171**, p. 1145; 1920, that manganese and silver salts affect the end point if potassium permanganate is titrated with arsenite in sulphuric acid solution.

The data in Table 1 show that it is optional whether the permanganate solution is titrated directly or reduced and oxidized. Furthermore, 1 g of iron introduces no significant differences.

On the basis of the preceding experiments the following procedure was then adopted for the determination of manganese in steel and iron. In this method as much as 20 mg of manganese can be used, and it is therefore possible to use 1 g samples in practically all cases. Some time after the method had been put in daily use at the Bureau of Standards it was learned that W. D. Brown,[17] of the Carnegie Steel Co., Duquesne, Pa., also uses a persulphate-arsenite method in which phosphoric acid is employed.

The results obtained by the recommended procedure are much better than those obtained heretofore on smaller samples by the ordinary persulphate method and are practically of the same order of accuracy as those obtained by the bismuthate method, which requires more time.

IV. RECOMMENDED PROCEDURE

1. SOLUTIONS REQUIRED

Acid mixture:	ml
Distilled water	525
Sulphuric acid (sp. gr. 1.84)	100
Phosphoric acid (85 per cent)	125
Nitric acid (sp. gr. 1.42)	250

Add the sulphuric acid to the water, mix and cool, add the nitric and phosphoric acids and again mix.

Silver nitrate (0.8 per cent):		
Silver nitrate	g	8
Distilled water	ml	1,000
Ammonium persulphate (25 per cent):		
Ammonium persulphate	g	[18] 25
Distilled water	ml	85

This solution deteriorates and should not be kept more than a few days.

Standard sodium arsenite solution approximately 0.03 N).—To 6 g of C. P. arsenic trioxide in a 600 ml beaker add 250 ml of water and 15 g of sodium hydroxide and stir until solution is complete. Saturate with carbon dioxide and dilute to 5 liters. Standardize as follows: Transfer 30 ml of the acid mixture to a 500 ml Erlenmeyer flask, add 100 ml of water, 10 ml of persulphate solution, 10 ml of silver nitrate solution, and boil for a minute to remove any nitrous fumes. Cool to room temperature, add 75 ml of water, exactly 20 ml of a standard 0.03 *N* potassium permanganate solution, and titrate with the sodium

[17] Private communication.

[18] Or necessary equivalent if strength is less than 95 per cent.

arsenite solution. The end point should be taken when the solution assumes a yellow green color which is not changed by the further addition of arsenite.

2. METHOD

To 1.000 g of the steel or iron (note 1) in a 500-ml Erlenmeyer flask add 30 ml of the acid mixture. Heat until solution is complete and boil until oxides of nitrogen have been expelled. Add 100 ml of cold water, 10 ml of the silver nitrate solution, and 10 ml of ammonium persulphate solution. Heat to boiling and boil briskly for one-half minute. Cool to 25° C. or lower, add 75 ml of cold water, and titrate with standard arsenite to a clear yellow end point [19] which does not change upon the addition of more arsenite.

3. NOTES

1. For cast irons dissolve as directed, filter off the graphite through a rapid paper, and wash with water. Dilute the filtrate, if necessary, to 125 ml and proceed as above.

2. If the operations are performed as directed, it is not necessary to make a preliminary oxidation of the solution.

3. Large amounts of chromium interfere because the yellow color of the chromate masks the pink color of the permanganic acid as the end point is approached. However, no particular difficulty was experienced when the amount of chromium did not exceed 15 mg.

4. Chrome-tungsten steels do not dissolve readily in the acid mixture. For such steels add 50 ml of dilute sulphuric acid (1:9) and 3 ml of phosphoric acid (85 per cent) to a 0.5 g sample and heat until action ceases. Add 40 ml of water, 10 ml of nitric acid (sp. gr. 1.20), and boil until tungsten carbides are all dissolved. Dilute, oxidize, etc., as for plain steel.

5. It is not desirable to incorporate the silver nitrate with the acid mixture because it tends to retard solution of some types of steels, more particularly certain nickel steels.

4. RESULTS OBTAINED

The performance of the method is illustrated by the results obtained in analyses of Bureau of Standards standard steels and in analyses of synthetic mixtures containing 1 g of electrolytic iron (manganese 0.002 per cent) and varying amounts of reduced 0.02 *N* potassium permanganate. These are shown in Tables 2 and 3.

[19] The color of the solution at the end point does not possess the green tint obtained in the absence of iron. However, the difference in shade is slight, and with a little practice the same end point can be obtained as in the absence of iron.

TABLE 2.—*Results obtained by applying the recommended method to the analysis of synthetic solutions prepared by dissolving 1 g of electrolytic iron and adding reduced 0.02 N $KMnO_4$ solution*

$KMnO_4$ solution [1] added	Mn present [2]	Arsenite solution required	Mn found	Error
ml	*Per cent*	*ml*	*Per cent*	*Per cent*
1.0	0.025	0.66	0.027	+0.002
		.64	.026	+.001
5.0	.117	2.88	.116	−.001
		2.95	.119	+.002
10.0	.232	5.78	.234	+.002
		5.77	.233	+.001
20.0	.462	11.55	.467	+.005
		11.52	.465	+.003
30.0	.692	17.12	.692	0
		17.18	.694	+.002
40.0	.922	22.84	.923	+.001
		22.80	.921	−.001
50.0	1.15	28.50	1.15	----------
		28.55	1.15	----------

[1] 1 ml of $KMnO_4$=0.000230 g of Mn.
[2] Manganese in the $KMnO_4$ plus that in the iron.

TABLE 3.—*Results obtained by applying the method to the analysis of Bureau of Standards standard steels*

Standard No.	Certificate value	Mn found	Difference	Type of steel
	Per cent	*Per cent*	*Per cent*	
35a	0.345	0.342	−0.003	A. O. H. 1 per cent carbon.
		.345	0	
16b	.381	.380	−.001	B. O. H. 1 per cent carbon.
		.380	−.001	
11c	.435	.436	+.001	B. O. H. 0.2 per cent carbon.
		.434	−.001	
8d	.482	.482	0	Bessemer 0.1 per cent carbon.
		.485	+.003	
23a	.634	.638	+.004	Bessemer 0.8 per cent carbon.
		.638	+.004	
10d	.915	.915	0	Bessemer 0.4 per cent carbon.
		.916	+.001	
33b	.700	.703	+.003	Nickel steel (3.5 per cent Ni).
		.706	+.006	
72	.651	.646	−.005	Chrome-molybdenum steel (0.91 per cent chromium, 0.15 per cent molybdenum).
		.652	+.001	
30b	.499	.493	−.006	Chrome-vanadium steel (1.00 per cent chromium, 0.21 per cent vanadium).
		.496	−.003	

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DETERMINATION OF FLUORINE AND OF SILICA IN GLASSES AND ENAMELS CONTAINING FLUORINE

By J. I. Hoffman, and G. E. F. Lundell

ABSTRACT

Methods for the determination of fluorine and of silica in the presence of each other remain practically the same as those developed by Berzelius over 100 years ago. These methods are very tedious and normally give low results for both fluorine and silica. In the new methods that are described, the procedure for separating silica and alumina from fluorine has been modified so that it is more accurate and takes less time, while the old method of determining fluorine as calcium fluoride has been replaced by the more rapid and equally accurate lead chlorofluoride method.

CONTENTS

	Page
I. Introduction	582
II. General discussion of methods of analysis	582
1. Silica	582
(*a*) Determination without regard to the effect of fluorine	582
(*b*) The use of boric oxide or arsenic trioxide to prevent loss of silica	582
(*c*) The method of Berzelius	583
2. Fluorine	584
(*a*) Methods involving the volatilization of fluorine as silicon tetrafluoride	584
(*b*) Precipitation as calcium fluoride in the presence of calcium carbonate	584
(*c*) Precipitation of calcium fluoride in the presence of calcium oxalate	584
(*d*) Volumetric determination of fluorine by titration with ferric chloride	585
(*e*) Other methods	585
III. Recommended methods of analysis	585
1. Preliminary discussion	585
(*a*) Drying the sample	586
(*b*) Fusion of the sample	586
(*c*) Separation of silica from fluorine	587
(*d*) Determination of silica	588
(*e*) Determination of fluorine	589
(*f*) Routine method for fluorine	591
2. Procedures	591
(*a*) Fusion of the sample and separation of silica from fluorine	591
(*b*) Determination of silica	592
(*c*) Determination of fluorine	592
(*d*) Routine method for fluorine	594
IV. Summary	595

I. INTRODUCTION

Many methods have been devised for the determination of fluorine in solutions of pure fluorides. Only a few of these can be applied to the analysis of such complex materials as glasses and enamels, and none of them gives satisfactory results. The same can be said concerning the determinations of silica in materials containing fluorine and silica, for silica can not be successfully determined unless it can be satisfactorily separated from fluorine.

II. GENERAL DISCUSSION OF METHODS OF ANALYSIS

1. SILICA

(a) DETERMINATION WITHOUT REGARD TO THE EFFECT OF FLUORINE

If an acid solution containing silica and fluorine is evaporated to dryness, some of the silicon is lost by volatilization as silicon tetrafluoride, SiF_4. The loss of silicon can not be calculated even if the quantity of fluorine present is exactly known because the loss varies with conditions and the amount that is lost is always less than that which is equivalent to the fluorine. Losses are greater in open than in covered vessels. Table 1 shows results that were obtained in determinations of silica in which the effect of fluorine was disregarded.

TABLE 1.—*Determination of silica without regard to the effect of fluorine* [1]

	Material	Method	Fluorine added	SiO_2	
				Present	Found
			Per cent	*Per cent*	*Per cent*
1	Soda-lime glass	Double dehydration with HCl	25	74.1	59.5
2		do	2	74.1	73.5
3		Double dehydration with $HClO_4$	10	74.1	70.9
4	do	Double dehydration with $HClO_4$ in a covered platinum dish	10	74.1	71.6
5		do	10	74.1	72.3

[1] The exact amounts of silica and fluorine in this case as well as in those to be mentioned in subsequent sections of this paper were known because the substances analyzed were synthetic mixtures of materials of known silica or fluorine content. The silica was usually added as Bureau of Standards soda-lime glass No. 80 and the fluorine as calcium fluoride of known purity or as sodium fluoride made by a modification of the method employed by D. J. McAdam and E. F. Smith (J. Am. Chem. Soc., **34**, p. 592; 1912) in their atomic weight work. In their method the hydrochloric acid in the hydrofluoric acid is removed by distilling from a solution containing an excess of potassium permanganate and discarding the first part of the distillate which contains the chlorine. In our work a purer hydrofluoric acid was obtained by adding about 0.5 g each of potassium fluoride and silver sulphate to 500 ml of a reasonably pure solution of hydrofluoric acid and distilling in a platinum still. The potassium fluoride "fixes" the silica as potassium fluosilicate, K_2SiF_6, and the silver sulphate forms insoluble silver chloride which is not decomposed in the distillation. The first 25 ml of distillate and the last 100 ml portion remaining in the still should be discarded. One such distillation yields hydrofluoric acid which is entirely free from hydrochloric acid and silica.

(b) THE USE OF BORIC OXIDE OR ARSENIC TRIOXIDE TO PREVENT LOSS OF SILICA

P. Jannasch and H. Weber [1] state that it is probable that if a fluorine-bearing silicate is fused with boric oxide at the temperature

[1] Ber. Deutsch. Chem. Gesell., **32**, p. 1670; 1899.

of the oxygen blast, all of the fluorine is volatilized as boron trifluoride, BF_3, without any loss of silica. All attempts on our part to verify this statement yielded low results for silica, but it is not certain whether silica was lost during the fusion or whether fluorine was incompletely volatilized and caused a loss of silica during the subsequent evaporation of the acidified solution. Silica is also lost if the determination is made by fusing with sodium carbonate, adding boric acid to the solution of the melt, and dehydrating with hydrochloric acid. Furthermore, if boric acid is present during the dehydration, the silica is always strongly contaminated by it, and treatment with methyl alcohol and hydrochloric acid does not entirely remove it. If it is not removed, it will count as silica for it is also volatilized by treatment with hydrofluoric acid.

The use of arsenious acid for the purpose of volatilizing the fluorine as arsenious fluoride, AsF_3, also yields incorrect results, for it was found not to prevent the formation of some silicon tetrafluoride, and the silica that is obtained is strongly contaminated by arsenic.

(c) THE METHOD OF BERZELIUS

The method of Berzelius [2] has stood for over 100 years and is still regarded as the standard procedure for separating silica from fluorine. It is long and tedious and gives results that are fairly accurate but usually low. The chief steps are as follows: The sample is decomposed by fusing with a mixture of sodium and potassium carbonates, the melt is extracted with water, the solution filtered, and the alumina and part of the silicic acid are separated from the fluorine in the water extract by precipitating with ammonium carbonate. The solution is then filtered and the rest of the silica removed by nearly neutralizing with successive small additions of nitric acid, boiling with an ammoniacal solution of zinc oxide, and filtering. The fluorine is determined in the filtrate by precipitating it as calcium fluoride. The silica is determined by evaporating to dryness the acid solution of the three residues (the water insoluble, the precipitate produced by ammonium carbonate, and that produced by the ammoniacal solution of zinc oxide). The precipitation with ammonium carbonate requires 12 hours, and the precipitate (if much silica is present, as in glasses) is extremely difficult to filter and wash. The subsequent neutralization with nitric acid, preparatory to the precipitation of the last of the silica by means of an ammoniacal solution of zinc oxide, is also time consuming, and the slightly alkaline filtrate obtained at the end of the operation usually holds from 1 to 2 mg of silica. In the analysis of a glass containing 9 per cent of fluorine an average of 73.6 per cent of silica was obtained by this method as compared with 74.1 per cent present. (See footnote under Table 1, p. 594.)

[2] J. J. Berzelius, Schweigg. J., **16**, p. 426; 1816; H. Rose, Ann., **72**, p. 343; 1849.

The use of mercuric oxide in preparing the precipitating reagent as recommended by F. Seemann [3] for recovering the last of the silica yields results which are slightly lower than those obtained when zinc oxide is used, even if the filtrate is neutralized and again evaporated as directed by Seemann. Moreover, the last of the mercury is not easily expelled from large silica residues.

2. FLUORINE

(a) METHODS INVOLVING THE VOLATILIZATION OF FLUORINE AS SILICON TETRAFLUORIDE

Glasses and enamels can not be decomposed by direct treatment with sulphuric or perchloric acid. It is obvious that methods involving the volatilization of fluorine as silicon tetrafluoride are impractical if a preliminary fusion is required to bring the material into solution. Even with soluble materials not all of the fluorine can be recovered by such a distillation. D. S. Reynolds, W. H. Ross, and K. D. Jacob [4] have shown that 92 per cent is about all that can be obtained by the best available procedures.

(b) PRECIPITATION AS CALCIUM FLUORIDE IN THE PRESENCE OF CALCIUM CARBONATE

It is practically impossible to filter freshly precipitated calcium fluoride. In the Berzelius method calcium fluoride is thrown down in neutral solution, together with some calcium carbonate. The mixture of these two precipitates can be filtered, but the fluoride must then be separated from calcium carbonate. This is done by first igniting at a low heat to get the fluoride into granular form and then treating the mixture with dilute acetic acid to leach out the carbonate. As many as four extractions with the dilute acetic acid are sometimes required. This always causes some solution of the fluoride, and a correction must be made for the amount that is dissolved. A further difficulty is caused by the presence of phosphates, vanadates, chromates, aluminum, and ammonium salts. All of these must be removed from the solution before the precipitation. The procedure will yield fairly accurate results, but it is long and tedious and requires strict attention to details. In the analysis of two glasses containing 9.93 and 5.75 per cent of fluorine (added as calcium fluoride), 9.74 and 5.77 per cent, respectively, were obtained by this method when all recoveries and solubility corrections were made.

(c) PRECIPITATION OF CALCIUM FLUORIDE IN THE PRESENCE OF CALCIUM OXALATE [5]

The coprecipitation of calcium fluoride and calcium oxalate is similar in many respects to the preceding method except that a known

[3] Z. anal. Chem., **44**, p. 343; 1905.
[4] J. Assoc. Official Agri. Chem., **11**, pp. 225–236; 1928.
[5] G. Starck and E. Thorin, Z. anal. Chem., **51**, p. 14; 1912.

quantity of a soluble oxalate is added instead of an unknown quantity of carbonate. The mixed precipitate is filtered, dried, and weighed, and the quantity of calcium fluoride is obtained by subtracting the weight of calcium oxalate equivalent to the amount of oxalate added. The precipitate is extremely difficult to filter and wash, but if this can be accomplished fairly accurate results are obtained, and the troublesome leaching with acetic acid is not required. In the analysis of two glasses containing 9.80 and 5.75 per cent of fluorine (added as calcium fluoride), 9.62 and 5.72 per cent, respectively, were obtained by this method.

(d) VOLUMETRIC DETERMINATION OF FLUORINE BY TITRATION WITH FERRIC CHLORIDE [6]

Titration of fluorine with a standard solution of ferric chloride involves the precipitation of iron cryolite, Na_3FeF_6, in a solution containing alcohol, a soluble fluoride, and a large excess of sodium chloride. Potassium thiocyanate is used as internal indicator. The chief objections to this method are the difficulty of judging the end point and the fact that practically all other substances except fluorine and sodium salts must be absent. An additional drawback is that 1 atom of iron is equivalent to 6 atoms of fluorine.

(e) OTHER METHODS

In our hands attempts to precipitate fluorine as barium fluosilicate, $BaSiF_6$, proved unsatisfactory because mixtures of barium fluoride and barium fluosilicate were precipitated. Attempts to precipitate thorium fluoride, ThF_4, were also unsatisfactory because mixtures of thorium fluoride and sodium thorium fluoride, Na_2ThF_6, were precipitated. This is in agreement with the observations of Adolph.[7] An attempt to precipitate fluorine as UF_4 by means of an excess of uranous sulphate (or chloride) also failed. The most promising of the methods used in the preliminary trials was that in which the fluorine is precipitated as lead chlorofluoride, PbClF. This method will be described in detail under methods of analysis.

III. RECOMMENDED METHODS OF ANALYSIS

1. PRELIMINARY DISCUSSION

After a careful consideration of the methods already described, it was decided that the Berzelius method or some modification of it would be the best for the separation of silica from fluorine. In the methods to be described the long precipitation period with ammonium

[6] See P. Guyot, Compt. rend., **71**, p. 274; 1870; and A. Greeff, Ber., **46**, p. 2511; 1913.

[7] In The Quantitative Methods for Fluorine, Thesis, University of Pennsylvania (1915) and Z. anal. Chem., **55**, p. 395; 1916: William H. Adolph gives a good account of a critical study of methods for the determination of fluorine.

carbonate, the difficult filtration of the precipitate, and the troublesome neutralization of the sodium carbonate are eliminated in the operations designed for the separation of silica from fluorine. Instead of precipitating the fluorine as calcium fluoride, it is precipitated as lead chlorofluoride which can be weighed or preferably, in this case, dissolved and the chlorine titrated.

(a) DRYING OF THE SAMPLE

Like most finely powdered substances glasses and enamels absorb some water upon standing in a moist atmosphere, but they offer little difficulty in drying or weighing. A sample ground to pass a No. 80 sieve and dried for one hour at 105° to 110° C. is satisfactory.

(b) FUSION OF THE SAMPLE

All of the orindary glasses and enamels are easily decomposed by fusing them at a moderate heat with sodium or potassium carbonate or a mixture of both. Silica need not be added to aid in the decomposition as the materials under discussion already contain enough. The use of the blast lamp is unnecessary, and even the full heat of the Tirrill burner is seldom required. It is only necessary that the mass be fluid, and it is preferable not to heat much beyond the temperature at which it melts. We have had no evidence of loss of fluorine during the fusion.[8]

Materials containing much silica, together with elements which form insoluble carbonates, as, for example, calcium, magnesium, or lead, when fused with sodium carbonate yield a cake which is quite difficult to disintegrate with hot water. This is especially true of many enamel mixtures. Potassium carbonate melts dissolve more readily, as has been pointed out in a discussion of the analysis of fluorspar,[9] and are entirely satisfactory.

Occasionally not all of the fluorine is recovered by extracting the melt with water, filtering, and washing the residue. In the present work very few of the residues showed as much as 1 mg of fluorine. To assure complete extraction Hillebrand [10] recommends that the insoluble residue be ignited and that the fusion and extraction be repeated. F. G. Hawley [11] recommends that the insoluble residue be boiled with a strong solution of sodium carbonate and then filtered to extract the last of the fluorine. This latter procedure is simple and entirely satisfactory if the original fusion was properly carried out. This treatment of the insoluble residue seldom yields appreciable amounts of fluorine and is only a precautionary measure.

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[8] F. G. Hawley (Ind. Eng. Chem., **18**, p. 573; 1926) found a considerable loss of fluorine when FeS_2 was present, but this must have been caused by roasting the sample of CaF_2 with FeS_2. In such a case sulphur is oxidized to sulphite or sulphate which replaces fluorine.

[9] G. E. F. Lundell and J. I. Hoffman, B. S. Jour. Research, **2**, p. 671; 1929.

[10] The Analysis of Silicate and Carbonate Rocks, U. S. Geol. Surv. Bull. No. 700.

[11] See footnote 8.

(c) SEPARATION OF SILICA FROM FLUORINE

When a sample of glass or enamel is fused with alkali carbonate, extracted with water, and filtered, some of the silica usually remains in the insoluble residue, but most of it passes into the filtrate with the fluorine, from which it must then be separated. In the methods usually employed aluminum and much of the silica are precipitated by adding ammonium carbonate to the solution, allowing it to stand for at least 12 hours, and filtering. The precipitate is very difficult to handle and often requires two or three hours to filter. The addition of large quantities of macerated paper does not materially expedite the filtration. It was found that an entirely satisfactory precipitate can be obtained in a few minutes by adding enough of a nitric acid solution of zinc nitrate to reduce the concentration of the sodium carbonate in the solution to about 1 per cent. The precipitate is bulkier than that obtained in the old method, but it is free from fluorine, contains nearly all of the silica and alumina,[12] and, above all, it is easily filtered and washed. The silica which still remains in solution is precipitated by neutralizing with nitric acid and boiling with an ammoniacal solution of zinc oxide.

Neutralization by successive small additions of nitric acid (as in the old method) is unnecessarily lengthy and troublesome and leaves the solution slightly alkaline, because not all of the sodium bicarbonate formed is destroyed. Such a solution usually holds from 1 to 2 mg of silica, and it is probably for this reason that most results for silica by the Berzelius method are low. By neutralizing the solution with dilute nitric acid until methyl red changes to a very delicate pink (pH about 5.6), and then boiling with a large excess of an ammoniacal solution of zinc oxide, all of the silica is recovered, and no fluorine is lost. A variation of 1 ml of *N* acid or alkali in this neutralization results in the loss of approximately 1 mg of silica regardless of whether fluorine is present or not. This is true because zinc silicate is soluble in solutions that are alkaline or contain ammonium salts. A little excess of nitric acid would be neutralized with ammonium hydroxide and leave its equivalent of ammonium nitrate in solution.

The use of mercuric oxide instead of zinc oxide as recommended by Seemann[13] yields slightly low results for silica even if the solution is strictly neutral to methyl red and no fluorine is present. The presence of fluorine has little or no effect on the precipitation whether zinc oxide or mercuric oxide is used. Greater losses of silica occur if the acidity or alkalinity of the solution is increased beyond the point of neutrality to methyl red before adding the ammoniacal solution of mercuric oxide.

[12] In a 0.5 g sample of glass containing 74 per cent of silica and 6 per cent of alumina, all but 8 per cent of the silica and 0.4 mg of the alumina were removed in this precipitation. The amount of silica left in solution varies somewhat but seldom is greater than that mentioned.

[13] See footnote 3, p. 596.

The results obtained by the different procedures for the recovery of small quantities of silica in the presence of fluorine are shown in Table 2. The precipitates obtained by the use of the zinc oxide reagent were dissolved in sulphuric acid and the silica determined by double dehydration as usual. The precipitates obtained by the use of the mercuric oxide reagent were directly ignited as recommended by Seemann. The weight of silica was then determined by treatment with hydrofluoric and sulphuric acids as usual. Seemann's directions do not clearly define the conditions of the solution prior to adding the ammoniacal solution of mercuric oxide, and it is possible that by proper adjustment of acidity or other conditions, the unfavorable results shown in Table 2 might be improved.

TABLE 2.—*Recovery of small quantities of silica in the presence of fluorine*

	Method of separating silica	Fluorine present	Other substances present	Condition of the solution in which silica was precipitated	Silica	
					Present	Found
		g			g	g
1	Boiling with an ammoniacal solution of zinc oxide.			Faint pink to methyl red (pH 5.6).	0.0184	0.0186
2	do	0.10		do	.0549	.0544
3	do	.05	0.1 g B_2O_3	do	.0737	.0736
4	do	.05	0.1 g B_2O_3	do	.0711	.0713
5	do	.10	0.1 g B_2O_3	do	.0228	.0230
6	do			Neutral to methyl red, then added 1 ml N-Na_2CO_3.	.0204	.0193
7	do			Between blue and yellow of brom phenol blue (pH 3.4).	.0269	.0244
8	Evaporating to dryness with an ammoniacal solution of mercuric oxide.			Faint pink to methyl red (pH 5.6).	.0084	.0055
9	do	.10		do	.0126	.0101
10	do			Neutral to methyl red then added 1 ml of N-Na_2CO_3.	.0115	.0069

(d) DETERMINATION OF SILICA

In the Berzelius method silica is determined by dissolving the insoluble residue and the ammonium carbonate and zinc oxide precipitates in hydrochloric acid and dehydrating in the usual manner. In the method to be outlined the residue and the two zinc precipitates are treated in like manner. If an appreciable amount of silica is present, yielding a bulky residue, the first dehydration with hydrochloric acid is easily accomplished on the steam bath. In the second dehydration not much silica is present, and the large quantity of zinc chloride forms a sirup which must be dehydrated on the hot plate. In the absence of large quantities of lead, calcium, or other substances which would form insoluble sulphates, it is preferable to substitute sulphuric acid in the second dehydration. Perchloric acid may be used in any case, but then the dehydration should be made in glass and 2 to 5 ml of nitric acid should be added to oxidize bits of filter paper or other reducing substances which might otherwise react violently with perchloric acid. However, hydrochloric

acid is decidedly to be preferred in the first dehydration [14] and sulphuric acid in the second.

Less than 1 mg of silica should escape the second dehydration, and this can be recovered by adding about 0.05 g of aluminum (as chloride) to the filtrate, precipitating with ammonium hydroxide, dissolving the precipitate in sulphuric acid, evaporating until fumes of the acid appear, diluting, and filtering. Sufficient ammonium chloride must be added to hold zinc in solution during the precipitation with ammonium hydroxide.

(e) DETERMINATION OF FLUORINE

The determination of fluorine in the filtrate from which the last of the silica has been removed by precipitation with an ammoniacal solution of zinc oxide is most satisfactorily made by precipitating the fluorine as lead chlorofluoride, PbClF. If obtained from pure solutions this precipitate may be collected on an asbestos pad, dried at 140° C., and weighed. In practice it is usually preferable to dissolve it in dilute nitric acid and determine the chlorine as in Volhard's method because the coprecipitation of small quantities of phosphates, chromates, sulphates, lead carbonate, and the like causes high results if the precipitate is weighed but has little or no effect if the chlorine is titrated. The precipitate is granular, settles very readily, and is easily filtered. Its solubility in water [15] (0.325 g per liter at 20° C.) upon first consideration might seem to bar its use in quantitative work, but satisfactory results are obtained if it is washed with a saturated solution of the salt. A precipitate washed with a saturated solution of lead chlorofluoride and cold water as described in the method below lost only 0.0024 g, corresponding to less than 0.2 mg of fluorine.

The composition of this precipitate can be varied by changing the conditions of precipitation, but C. Sandonnini [16] has shown by thermal analysis that lead chlorofluoride is a true compound and not a mixture of PbF_2 and $PbCl_2$. Precipitates of the proper composition may be obtained by balancing such variables as volume and acidity of the solution, concentration of lead and chloride ions, temperature, time of standing, etc. The conditions prescribed in the method below are not the only ones which might yield correct results. For instance, higher concentrations of lead and chloride ions, together with higher acidity may yield equally accurate results. Most analysts [17] differ as to these conditions. Those prescribed in this

[14] Large quantities of silica obtained by dehydrating with sulphuric or perchloric acid under the conditions which obtain in this dehydration hold carbon very tenaciously upon ignition. The reason is not apparent, but it is extremely difficult to obtain silica which is white. Slow ignition in the beginning is essential.

[15] G. Starck, Z. anorg. Chem., **70**, p. 173; 1911.

[16] Atti. R. Accad. Lincei, **20**, p. 172; 1911.

[17] See reference in footnote 8, p. 598, and footnote 15, above; also L. D. Hammond, Ind. Eng. Chem., **16**, p. 938; 1924.

paper can be duplicated easily by different operators. Reasonable duplication is necessary for correct results. For example, the lead nitrate and sodium acetate should be weighed to 0.1 g. The pH value of the solution after adding the sodium acetate is about 5. At this acidity fluorine causes no trouble, and glass vessels may be used for the precipitation.

The presence of aluminum, iron, large quantities of alkali salts, and boric oxide retard or prevent the complete precipitation of lead chlorofluoride. Of these, the first two are by far the most troublesome, probably because they form cryolites which are more stable than lead chlorofluoride. The effect of the last two can be minimized by letting the solution stand for a longer time and is not serious with the quantities usually encountered in the analysis of glasses and enamels. Boron has a greater effect when the quantity of fluorine is large than when it is small. In the method to be described, the effect is small and can usually be disregarded in the analysis of glasses or enamels if the amount of fluorine involved lies between 0.01 and 0.03 g. Above 0.03 g its effect becomes more noticeable. The effect of these substances is shown in Table 3.

TABLE 3.—*Determination of fluorine in synthetic solutions by precipitation as PbClF and titration of chlorine*

	Contaminants	Fluorine	
		Present	Found
		g	*g*
1		0.0149	0.0151
2	5 g Na_2CO_3	.0149	.0147
3	do	.0747	.0749
4	10 g Na_2CO_3	.0149	.0144
5	do	.0149	.0141
6	10 g K_2CO_3	.0149	.0143
7	5 g Na_2CO_3+0.06 g B_2O_3	.0299	.0298
8	5 g Na_2CO_3+0.11 g B_2O_3	.0747	.0721
9	5 g Na_2CO_3+0.3 g B_2O_3	.0747	.0621
10	5 g Na_2CO_3+0.3 g B_2O_3	.0149	.0143
11	5 g Na_2CO_3+0.3 g B_2O_3	.0149	.0144
12	5 g Na_2CO_3+0.001 g Al_2O_3	.0149	.0133
13	5 g Na_2CO_3+0.001 g Al_2O_3	.0149	.0138
14	5 g Na_2CO_3+0.005 g Al_2O_3	.0149	.0127
15	5 g Na_2CO_3+0.05 g Fe_2O_3	.0149	<.01
16	5 g Na_2CO_3+0.03 g SiO_2	.0149	.0146
17	5 g Na_2CO_3+0.03 g SiO_2	.0149	.0150
18	5 g Na_2CO_3+0.5 g NH_4NO_3	.0149	.0149
19	5 g Na_2CO_3+3.0 g NH_4NO_3	.0149	.0139
20	5 g Na_2CO_3+0.02 g P_2O_5	.0149	.0153
21	5 g Na_2CO_3+0.1 g H_2SO_4	.0487	.0491
22	5 g Na_2CO_3+0.05 CrO_3	.0288	.0291

The results in Table 3 were obtained by direct determinations in synthetic solutions by procedure (*c*) below and did not involve a preliminary fusion. It is apparent that small quantities of silica, ammonium nitrate, phosphoric acid, sulphuric acid, and chromic acid

have little or no harmful effect if lead chlorofluoride is precipitated under the conditions prescribed, and the chlorine is titrated as in Volhard's method. Phosphates, sulphates, and chromates are precipitated, at least in part, with lead chlorofluoride but are harmful only so far as they may carry down chlorides. The positive error from this source is apparently slight. Lead phosphate if thrown down with lead chlorofluoride, creeps through the filter, but this has no effect upon the result.

(f) ROUTINE METHOD FOR FLUORINE

If fluorine alone is to be determined, the careful separation of silica from fluorine need not be made, and the time required for a fluorine determination can be materially reduced by omitting the digestion of the first insoluble residue and the precipitation with ammoniacal zinc oxide solution. Such a modification is described in procedure (*d*) below.

2. PROCEDURES

(a) FUSION OF THE SAMPLE AND SEPARATION OF SILICA FROM FLUORINE

Fuse 0.5000 g of the sample (dried at 105° C.) with 5 g of sodium or potassium carbonate or a mixture of both, leach the cooled melt with hot water, and filter when disintegration is complete. Return the insoluble residue to the dish by the use of a jet of water, add 50 ml of a 2 per cent solution of sodium carbonate, boil for a few minutes, filter, and wash thoroughly with hot water.[18] Reserve the residue (1) for the determination of silica. To the combined filtrates, which should have a volume of approximately 300 ml, add 1 g of zinc oxide dissolved in 20 ml of dilute nitric acid (1:9),[19] boil for one minute, filter, and wash the residue thoroughly with hot water. Reserve the precipitate (2) for the determination of silica. Add a few drops of methyl red indicator solution to the filtrate, nearly neutralize with nitric acid, and evaporate to a volume of 200 ml, taking care that the solution remains alkaline during the evaporation. Finish the neutralization of the concentrated solution by adding dilute nitric acid (1:9) until the color is a very faint pink. Now add 1.0 g of zinc oxide dissolved in ammonium hydroxide and ammonium carbonate,[20] and boil in a covered platinum dish until the odor of ammonia is entirely gone. This usually requires boiling until the volume of the solution has been reduced to about 50 ml. After all of the ammonia is expelled,

[18] Boiling with a solution of sodium carbonate aids in completely extracting the fluorine from the insoluble residue, but is not necessary in routine work if the melt has been well disintegrated at the start.

[19] This denotes 10 ml of nitric acid (sp. gr. 1.42) mixed with 90 ml of water. This system of designating dilute acids is used throughout this paper. If no dilution is specified, the concentrated reagent is intended.

[20] Transfer 1.0 g of zinc oxide and 2.0 g of ammonium carbonate to a small beaker, add 20 ml of water and 2 ml of ammonium hydroxide (sp. gr. 0.90), and digest on the steam bath until a clear solution is obtained.

add about 50 ml of warm water, stir, allow to stand for a few minutes, filter, and wash the precipitate (3) with cold water. Reserve the filtrate (4).

(b) DETERMINATION OF SILICA

With the aid of a jet of dilute hydrochloric acid (5:95) transfer the insoluble residue (1) and the two zinc precipitates (2 and 3) from the papers to the dish in which the last precipitation was made. Ignite all papers used in the preceding filtrations, and add any residue so obtained to the contents of the dish. Now add 25 ml of hydrochloric acid and evaporate to dryness on the steam bath. Remove the dish from the steam bath, drench the residue with 10 ml of hydrochloric acid, and then add 100 to 150 ml of hot water. Digest on the steam bath for 15 minutes, filter, and wash thoroughly with hot dilute hydrochloric acid (5:95) and then with hot water. Return the filtrate and washings to the dish in which the evaporation was made, add 10 ml of sulphuric acid,[21] and evaporate until fumes of sulphuric acid are evolved. Allow to cool, add 100 to 150 ml of warm water, digest for a few minutes until salts are in solution, filter, and wash with hot water. Place the two papers containing the silica in a weighed platinum crucible, heat slowly until dry, next char the paper without inflaming, burn off the carbon at as low a temperature as possible, and finally ignite at about 1,200° C. Cool in a desiccator, weigh, and repeat the heating until a constant weight is obtained. Determine the silica by treatment with hydrofluoric and sulphuric acids in the usual manner.

To recover the silica left in the filtrate after the second dehydration, add about 0.05 g of aluminum (in the form of chloride) and 10 to 15 g of ammonium chloride, and precipitate the aluminum with ammonium hydroxide. Filter and dissolve the precipitate in 50 ml of dilute sulphuric acid (1:9), dehydrate, filter, and add the small quantity of silica to that obtained above.[22]

(c) DETERMINATION OF FLUORINE

To the filtrate (4) add two drops of brom phenol blue[23] indicator and 3 ml of a 10 per cent solution of sodium chloride. Adjust the volume of the solution to 250 ml, add dilute nitric acid until the color changes to yellow, and then add dilute sodium hydroxide until it

[21] 25 ml of 60 to 70 per cent perchloric acid may be substituted for the sulphuric acid, but then 2 to 5 ml of nitric acid should be added and the dehydration carried out in glass.

[22] This recovery usually amounts to less than 1 mg of silica and may be omitted in routine work if the previous operations have been properly performed.

[23] To prepare the brom phenol blue indicator solution grind the dry powder thoroughly with a sodium hydroxide solution (1.5 ml of 0.1 *N* sodium hydroxide for 0.1 g of powder) and dilute to make a 0.4 per cent solution.

changes just to blue. Now add 2 ml of dilute hydrochloric acid (1:1) and 5.0 g of solid lead nitrate, $Pb(NO_3)_2$, and heat on the steam bath. As soon as the lead nitrate is in solution, add 5.0 g of solid sodium acetate,[24] $NaC_2H_3O_2+3H_2O$, stir vigorously, and digest on the steam bath for one-half hour with occasional stirring. Allow to stand over night [25] at room temperature and decant the solution through a paper of close texture (No. 589 S and S blue band or No. 42 Whatman). Wash the precipitate, beaker, and paper once with cold water, then four to five times with a cool saturated solution of lead chlorofluoride [26] and then once more with cold water.

Transfer the precipitate and paper to the beaker in which the precipitation was made, stir the paper to a pulp, add 100 ml of dilute nitric acid (5:95), and heat on the steam bath until the precipitate is dissolved (five minutes is ample). Then add a slight excess of a 0.2 *N* solution of silver nitrate,[27] digest on the steam bath for one-half hour, cool to room temperature while protected from the light, filter, wash with cold water, and determine the silver nitrate in the filtrate by means of a standard solution of potassium thiocyanate,[28] using 5 ml of a solution of ferric alum as the indicator.[29] Subtract the amount of silver nitrate found in the filtrate from that originally added. The difference will be that required to combine with the chlorine in the lead chlorofluoride, and from this the fluorine may be computed. One ml of 0.2 *N* silver nitrate is equivalent to 0.00380 g of fluorine.

The method as written holds well between the limits of 0.01 to 0.1 g of fluorine. Below 0.01 g the results have a tendency to be slightly low and above 0.1 g they tend to be slightly high.

Typical results obtained by the method are shown in Table 4.

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[24] If a good grade of sodium acetate is not available, prepare a solution as follows: Add 300 g of sodium bicarbonate to about 205 ml of glacial acetic acid, dilute to about 500 ml with water, and heat on the steam bath until frothing ceases. Cool the solution, and dilute it to 1 liter. The final solution should give an acid reaction with methyl red. 10 ml of this solution is equivalent to approximately 5 g of sodium acetate, $NaC_2H_3O_2+3H_2O$.

[25] Four hours is sufficient in routine work unless much boron is present.

[26] To prepare lead chlorofluoride wash solution: (*a*) Dissolve 10 g of lead nitrate in 200 ml of water; (*b*) dissolve 1.0 g of sodium fluoride in 100 ml of water and add 2 ml of concentrated hydrochloric acid; and, (*c*) mix solutions (*a*) and (*b*). Allow the precipitate to settle and decant the supernatant liquid. Wash four or five times with 200 ml of water by decantation, and then add about 1 liter of cold water to the precipitate and allow to stand for one hour or longer with occasional stirring. Pour through a filter and use the clear filtrate. By adding more water to the precipitate of lead chlorofluoride in the beaker and stirring, more wash solution may be prepared as needed.

[27] Standardized by precipitating a measured portion with hydrochloric acid and weighing the silver chloride.

[28] Standardized by comparing with the standard solution of silver nitrate under the same conditions as obtain in the method. A convenient concentration is 0.1 *N*.

[29] A cold saturated water solution of ferric alum (free from chlorides) to which has been added sufficient colorless nitric acid to bleach the brown color of the water solution.

TABLE 4.—*Results obtained by the use of procedures (b) and (c)*

[All results are calculated on the basis of a 0.5 g sample]

	Material	Fluorine		Silica		Other substances present
		Present	Found	Present	Found	
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
1	Synthetic mixture	6.00	6.06	74.1	n. d.	Al_2O_3, 6; TiO_2, 0.3.
2	do	7.24	7.36	73.9	73.9	Al_2O_3, 6; TiO_2, 0.3.
3	do	7.24	7.20	79.1	79.1	Do.
4	do			10.98	10.82	Na+K salts+Al_2O_3, 10.
5	do	2.0	n. d.	7.54	7.40	Do.
6	do	10.0	n. d.	14.74	14.72	Na+K salts+B_2O_3, 11.
7	do	10.0	n. d.	14.22	14.26	Do.
8	do	2.1	2.2	23.9	24.0	$Ca_3(PO^4)_2$, 10; Sb_2O_3, 8; B_2O_3, 20.
9	do	5.7	5.6	67.3	67.4	Al_2O_3, 6; B_2O_3, 20; CoO, 2; MnO_2, 4; NiO, 2; SnO_2, 10; Sb_2O_3, 4.
10	do	10.4	10.4	51.2	51.4	PbO, 13; B_2O_3, 11; Sb_2O_3, 4; BaO, 2.
11	do	10.1	9.9	57.5	57.4	Al_2O_3, 3; $MgCO_3$, 10; B_2O_3, 11.
12	do	2.1	2.1	57.6	57.5	Al_2O_3, 8; PbO, 13; B_2O_3, 3; Sb_2O_3, 2; SnO_2, 2.
13	do	2.7	2.6	50.0	n. d.	Sb_2O_3, 4; $Ca_3(PO_4)_2$, 6; B_2O_3, 20.
14	do	5.2	5.2	66.0	n. d.	B_2O_3, 20; CoO, 2; MnO_2, 4; NiO, 2; Al_2O_3, 6.
15	do	19.8	19.3	60.0	n. d.	B_2O_3, 11; Sb_2O_3, 4.
16	Opal glass [1]	[2] 5.75	5.63	[2] 67.6	67.6	
17	do	[2] 5.75	5.75	[2] 67.6	67.6	
18	do	[2] 5.75	5.71	[2] 67.6	n. d.	
19	do	[2] 5.75	5.74	[2] 67.6	n. d.	
20	do	[2] 5.75	5.69	[2] 67.6	n. d.	
21	Phosphate rock	5.02	2.76			
22	do	5.02	3.34			

n. d.=not determined.

[1] W. F. Muehlberg, chief chemist of the Newburgh Steel Works, Cleveland, Ohio, reported 5.61 per cent of fluorine and 67.8 per cent of silica on this glass the first time he used the procedures (*b*) and (*c*) as written. On a reanalysis he reported 5.70 per cent of fluorine and 67.6 per cent of silica.

[2] Certificate value of Bureau of Standards' sample of opal glass No. 91. These figures were obtained by averaging the results of four cooperating analysts using different types of approved methods. The figure for fluorine may be subject to an error of ±0.05 per cent.

(d) ROUTINE METHOD FOR FLUORINE

Fuse 0.5000 g of the sample (dried at 105° C.) with 6 g of potassium carbonate, leach the cooled melt with hot water, and filter when disintegration is complete. Wash the insoluble residue thoroughly with hot water, and adjust the volume of the filtrate and washings to approximately 200 ml. Add 1 g of zinc oxide dissolved in 20 ml of dilute nitric acid (1:9), boil for one minute with constant stirring, filter, and wash thoroughly with hot water. Proceed as in (*c*), determination of fluorine (above).

Typical results obtained by the use of the routine method are shown in Table 5.

TABLE 5.—*Results obtained for fluorine by the routine method (d)*

(All results are calculated on the basis of a 0.5 g sample)

	Material	Fluorine		Other substances present
		Present	Found	
		Per cent	*Per cent*	*Per cent*
1	Opal glass	5.75	5.68	
2	do	7.12	7.02	
3	do	5.75	5.83	
4	do	5.75	5.70	FeS_2, 10.
5	do	5.75	5.82	CrO_3, 10.
6	do	5.75	5.59	$MgCO_3$, 20.
7	Synthetic mixture [1]	2.3	2.0	Al_2O_3, 6; B_2O_3, 11; Sb_2O_3, 4; SnO_2, 4; $MgCO_3$, 6.
8	do	4.8	4.7	Al_2O_3, 6; B_2O_3, 20; PbO, 13; BaO, 2.
9	do	2.3	2.1	Al_2O_3, 6; B_2O_3, 11; Sb_2O_3, 4; SnO_2, 4; $MgCO_3$, 6.
10	do	2.3	2.2	Al_2O_3, 6; B_2O_3, 11; Sb_2O_3, 4; SnO_2, 4; $MgCO_3$, 2.

[1] Bureau of Standards soda lime glass No. 80 to which were added the constituents noted.

IV. SUMMARY

1. Various methods of determining silica in the presence of fluorine have been tested, but only the procedure developed by Berzelius or some modification was found to be reliable. In the methods described the procedure of Berzelius is modified so as to eliminate (1) the long precipitation period with ammonium carbonate and the difficult filtration which follows; and (2) the slow and troublesome neutralization with small portions of nitric acid.

2. It was found that for quantities of fluorine between 0.01 and 0.10 g the precipitation of fluorine as lead chlorofluoride is much more convenient and rapid, and as accurate as the precipitation of a mixture of calcium fluoride and calcium carbonate followed by extraction of the latter with acetic acid.

3. The lead chlorofluoride method succeeds in the presence of moderate quantities of ammonium nitrate, and boric, chromic, sulphuric or phosphoric acids, but as now written, it is not suitable for determining fluorine in phosphate rock. The presence of much magnesium tends to yield slightly low results.

4. The effects of various other contaminants, such as oxides of tin, antimony, iron, aluminum, nickel, cobalt, manganese, and lead, are shown, and a routine method for determining fluorine is given.

WASHINGTON, June 8, 1929.

THE HEAT OF FORMATION OF SULPHUR DIOXIDE

By J. R. Eckman[1] and Frederick D. Rossini

ABSTRACT

The heat of formation of sulphur dioxide has been redetermined. Since the burning of sulphur in excess oxygen results in the formation of varying small amounts of sulphur trioxide, which evolves some 90,000 more joules per mole in its formation than does sulphur dioxide, the difficulties involved in analyzing the combustion products for the trioxide and in making the corresponding corrections were obviated by the use of a specially designed calorimetric reaction chamber in which oxygen reacts with an excess of hot sulphur vapor to form pure sulphur dioxide. The heat of formation of sulphur dioxide at 25° C. from rhombic sulphur and gaseous oxygen was found to be $+296{,}890 \pm 200$ absolute joules per mole.

CONTENTS

	Page
I. Introduction	597
II. The reaction chamber and its operation	599
III. The chemical procedure	601
1. Preparation of the sulphur	601
2. Purification of the oxygen and the nitrogen	601
3. The analytical methods	602
IV. The calorimetric apparatus and accessory instruments	603
1. The calorimeter	603
2. The thermometer	605
3. The electrical energy system	606
V. Molecular weights, constants, factors, units, etc	608
VI. The calorimetric procedure	609
1. Calibration experiments	609
2. Sulphur dioxide experiments	612
VII. Results	615
VIII. Summary	618

I. INTRODUCTION

The thermochemical data of J. Thomsen and M. Berthelot, who, working independently, laid the foundations of modern thermochemistry by their prodigious work of nearly half a century ago, are in many cases in good agreement. One striking exception to this consistency, however, occurs in the case of their results on the heat of formation of SO_2. Berthelot[2] reported a value of $+69{,}260$ calories

[1] The bureau regrets to announce that since this paper was written Doctor Eckman has died.

[2] M. Berthelot, Ann. de chim. et de phys., **28**, p. 422; 1881.

while Thomsen[3] found +71,080 calories. The discrepancy is 2½ per cent. This difference is much greater than can be accounted for by the random errors in their calorimetric technic, and may be the result of some fault in the analytical methods.

Although their experimental methods were slightly different, both Thomsen and Berthelot burned the sulphur in an excess of oxygen. This resulted in the formation of varying small amounts of SO_3 along with the SO_2, and, since the heat of formation of SO_3 is about 21,500 calories per mole greater than that of SO_2, it was necessary to determine the exact amount of SO_3 formed in each experiment so that the proper correction could be applied. Another possible correction to such experimentally determined heats is that for the heat of the reaction of the SO_3 with water vapor from imperfectly dried oxygen or with moisture on the walls of the apparatus.

Thomsen and Berthelot did not agree as to the effectiveness of each other's analytical methods for determining the SO_3 formed. Berthelot,[4] in his second report on the heat of formation of SO_2, which appeared shortly after Thomsen[5] had published his results, was of the opinion that Thomsen's higher value was due to the fact that his analytical method did not recover all the SO_3 formed.

Berthelot[4] quoted results by five earlier investigators. These included the following, in chronological order: Dulong, + 83,200; Hess, + 82,200; Favre and Silbermann, +71,200; Andrews, +73,800; Thomsen, +71,080; and finally Berthelot, +69,260 calories. The results of Dulong and of Hess are obviously much in error, since all the others are grouped within about 5 per cent of one another. In 1904, Giran reported a value of 69,800 calories.[6]

Before attempting a new calorimetric determination of the heat of this reaction there were two problems to solve. The first of these was the development of a sufficiently exact method for determining small amounts of SO_3 in SO_2. The solution of this problem is reported in a previous paper by one of the authors.[7] The method consists, briefly, in condensing the SO_3 from the SO_2, dissolving it in an oxygen-free aqueous solution of $BaSO_3$, and weighing the precipitated $BaSO_4$. The second problem involved the development of a satisfactory calorimetric reaction chamber in which the union of sulphur and oxygen could be made to take place with the formation of a minimum amount of SO_3.

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[3] J. Thomsen, Thermochemische Untersuchungen, J. A. Barth, Leipzig; 1882. Berichte, **13A**, p. 959; 1880.

[4] See footnote 2, p. 597.

[5] See footnote 2, p. 597.

[6] H. Giran, Compt. rend., **139**, p. 1219; 1904; **140**, p. 1704; 1905. With a bomb calorimeter Giran found that the apparent heat of formation of 1 mole of SO_2, after correction for the formation of SO_3, increased with increase in the pressure of the oxygen in the bomb. He offered as an explanation for this the formation of $H_2SO_4.SO_3$ from the reaction of SO_3 with the small amount of water vapor present in the bomb.

[7] J. R. Eckman, B. S. Sci. Paper No. 554, **22**, p. 277; 1927.

II. THE REACTION CHAMBER AND ITS OPERATION

The fundamental idea underlying the design and construction of the reaction chamber was the introduction of oxygen gas into an excess of hot sulphur vapor, in order to minimize the formation of SO_3.[8] After preliminary experiments with various types, the reaction chamber shown in Figure 1 was developed. In this reaction chamber, sulphur is converted into SO_2 without the formation of any detectable amounts of SO_3 when tested by the analytical method described above.

The reaction chamber was made entirely of pyrex glass with the exception of the platinum wire used to supply electrical energy to the chamber and the platinum tip on the inlet tube.

The procedure employed in carrying out the reaction, with the chamber immersed in the water of the calorimeter, was as follows: About 8 g of pure rhombic sulphur, broken up into very small pieces, was introduced into the space *C* through the entry tube *D*. The close-fitting ground-glass cap at *D* was sealed with de Khotinsky cement. Pure dry nitrogen gas was passed through the reaction chamber, entering at *L* and leaving at *M*, until all the space in the chamber was filled with nitrogen. Then an electric current was sent through the platinum wire. The heat developed melted all of the sulphur and vaporized part of it. The energy required to accomplish this totaled about 4,800 joules, over a period of four minutes. One-half minute before the current was cut off, the flow of pure dry oxygen gas into the chamber through *L* was started. When the oxygen came in contact with the hot sulphur vapor, the formation

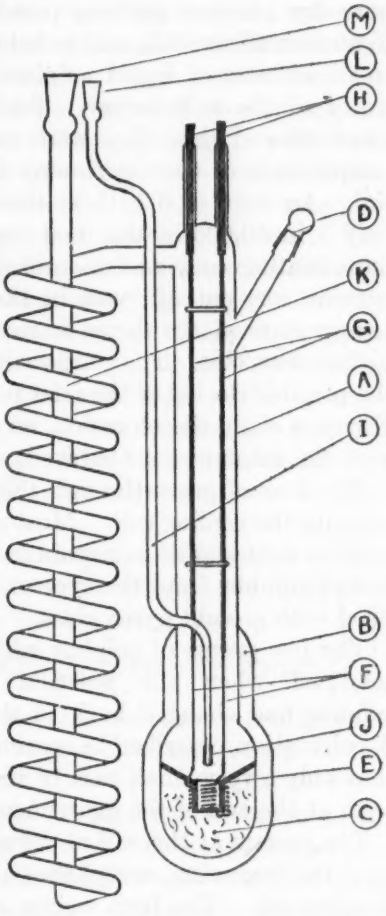

FIGURE 1.—*The reaction chamber*

A, body; *B*, vacuum jacket; *C*, space containing the sulphur which is filled in through the tube *D*; *E*, open cylindrical tube, with supports to wall, for carrying the heating coil of platinum wire; *F*, No. 29 platinum wire; *G*, No. 18 platinum wire; *H*, No. 14 platinum wire; *I*, gas inlet tube with platinum tip *J*; *K*, coil for cooling exit gases; *L* and *M* ground glass connections. Over-all length is 24 cm

[8] This method of preparing SO_2 has been used by Randall and Bichowsky, J. Am. Chem. Soc., **40**, p. 368; 1918.

of SO_2 commenced. The visible evidence of this reaction was a blue-green region several centimeters long at *J*. The SO_2 escaped from the body of the chamber into the cooling coil and passed through the exit *M* into an absorber. When a sufficient amount of sulphur had been converted into SO_2, the flow of oxygen was stopped and pure dry nitrogen gas was passed through the system. This served to remove all the SO_2, and to help cool the chamber with its remaining small amount of liquid sulphur by conducting heat energy to the water of the calorimeter. Temperature measurements of the exit gases showed that they were cooled, within 0.1° or 0.2° C., to the temperature of the calorimeter in their passage through the cooling coil. An error of 0.2° C. in this measurement makes a difference of only 1 in 50,000 in the final result. The temperature of the platinum heating coil, as determined from its resistance just before the current was cut off, was in the neighborhood of 500° C., and the temperature of the flame or reaction region proper must have been higher than this. The purpose of the platinum tip *J* was to prevent the possible closing of the inlet tube by the sealing action of the flame. Except a slight discoloration, no evidence of any reaction of platinum with the sulphur was observed.

The flow of gases through the system carried some sulphur vapor out into the cooling coil. Most of this condensed in the coil, but some sulphur dust tended to remain in the gas stream. To prevent possible loss of sulphur from the system, several inches of the exit tube was filled with ground pyrex glass.

The few grams of sulphur which remained in the space *C* quickly solidified when the reaction was stopped, and most of the sulphur had changed back to the rhombic form within 30 minutes. A calculation described in section 2, Part VI, of this paper indicates that only a very small part of the sulphur remained in the monoclinic form at the end of the experiment.

The system at the end of the experiment was in the same condition as at the beginning, except that all but a few grams of the sulphur had disappeared. The heat energy resulting from the conversion of this sulphur into SO_2 had raised the temperature of the calorimeter several degrees.

Quantitative tests showed that no SO_3 was formed when the reaction was carried out with an oxygen flow ranging from 0.05 to 0.15 liter per minute. In one test, SO_3 vapor was purposely introduced into the reaction chamber with the oxygen gas and must have been there reduced to SO_2 since no SO_3 could be detected in the exit gases.

III. THE CHEMICAL PROCEDURE

1. PREPARATION OF THE SULPHUR

The first step in the preparation of the pure sulphur for this investigation was its precipitation from an aqueous solution of $Na_2S_2O_3$ with HCl. Crystallized $Na_2S_2O_3.5H_2O$ was dissolved in twice its weight of water and an equivalent amount of concentrated HCl solution was added with constant stirring. When most of the sulphur had settled, the supernatant liquid was poured off and the sulphur was filtered out by suction on a porous porcelain plate in a Büchner funnel. The sulphur was then repeatedly washed with distilled water.

After drying, this sulphur was transferred to one of three pyrex flasks sealed in series so as to constitute a double glass still. The last traces of water were removed by heating the sulphur in flask 1 for some time below its melting point and removing the vapors with a vacuum pump. The sulphur was then melted and distilled, in vacuo, into flask 2, and then from flask 2 to flask 3. In the line between the last flask and the pump was a tube containing P_2O_5. This sulphur was then broken up into small pieces, placed in another multiple still, and redistilled four times in vacuo. The final pure sulphur was stored in a desiccator containing P_2O_5 and an atmosphere of pure nitrogen.

The liquid obtained by leaching several samples of this sulphur with warm water was tested [9] for both sulphuric and polythionic acids with negative results.

2. PURIFICATION OF THE OXYGEN AND THE NITROGEN

The oxygen and nitrogen purification trains are shown in Figure 2. Numbers are placed on parts of the oxygen line and letters on the nitrogen line.

The oxygen line consists of: (1) A cylinder containing oxygen; (2) an electric furnace for heating to 800° to 900° C. a tube containing platinized quartz and palladinized asbestos, which catalyzed the oxidation of the hydrogen in the oxygen; (3) a tube containing "dehydrite" ($Mg(ClO_4)_2.3H_2O$) and P_2O_5 for removing the moisture in the gas; (4) a mercury flow meter.

The nitrogen line consists of: *A*, a cylinder containing nitrogen; *B*, *C*, a bottle and a spiral each containing an aqueous solution of NH_4OH and NH_4Cl in contact with copper filings, for removing the oxygen from the nitrogen;[10] *D*, *E*, *F*, towers containing dilute to concentrated H_2SO_4 to remove NH_3; *G*, a tube containing "ascarite" (a mixture of hydrated NaOH and asbestos) for removing any CO_2 present, and "dehydrite" for removing moisture; *H*, *J*, tubes con-

[9] J. W. Mellor, Modern Inorganic Chemistry, Longmans, Green & Co., p. 458; 1916.
[10] W. L. Badger, J. Ind. Eng. Chem., 13, p. 161; 1920.

taining "dehydrite" and P_2O_5, respectively, for removing the last traces of moisture from the nitrogen; *K*, a mercury flow meter.

3. THE ANALYTICAL METHODS

The amount of sulphur which was converted to SO_2 in any given experiment was determined by weighing the reaction chamber before and after the experiment. The procedure was as follows: The necessary amount of sulphur, 6 to 8 g, was placed in the chamber. Pure dry nitrogen gas was passed through the chamber for about half an hour. Then the chamber was stoppered and weighed. When the experiment was completed, the chamber was again filled with nitrogen in the same manner as before, and weighed. The exterior of the glass chamber was thoroughly cleaned with ether and dried before each weighing. The total weight of the chamber was about 130 g, and the weighings were made to 0.0001 g. The apparent weight of the sulphur which had been used up in the experiment was corrected to vacuum by multiplying by the factor 1.00044.

As a check on the amount of sulphur burned as determined by direct weighing, the amount of SO_2 formed in the experiment was determined by absorbing it in "ascarite." The exit gases from the calorimeter were passed through a cylindrical glass tube, 4 cm in diameter and 23 cm tall, containing the "ascarite," together with a layer of "dehydrite" or P_2O_5 at the exit end. In order to avoid plugging the absorber and consequent stoppage of the gas flow, the "ascarite" was thoroughly mixed with an equal volume of pumice stone of the same mesh. The absorber was provided with ground-glass stoppers. A guard tube containing the same drying agent was attached to the exit end of the absorber during the experiment to prevent back diffusion of moisture from the air.

Initial experiments were made with known amounts of SO_2 to determine whether the "ascarite" would absorb it completely. This was found to be the case within the limits of error of the vacuum correction which must be applied to the apparent weight of the SO_2 absorbed. The absorber was always filled with pure dry nitrogen and closed at atmospheric pressure before each weighing.

The determination of the vacuum correction to be applied to the apparent weight of SO_2 required a knowledge of the change in volume of the "ascarite" which accompanied the absorption of the SO_2. For this purpose the assumption was made that the product formed in the absorber was $NaHSO_3$, formed by the reaction of equimolal amounts of NaOH and SO_2. Calculated on this basis, the increase in volume of the solid in the absorber per gram of SO_2 absorbed was the difference in the volume of 1 mole of $NaHSO_3$ and 1 mole of NaOH divided by the molecular weight of SO_2. The weight of this volume of nitrogen at the pressure and temperature to which it was subject

FIGURE 2.—*Oxygen and nitrogen lines*

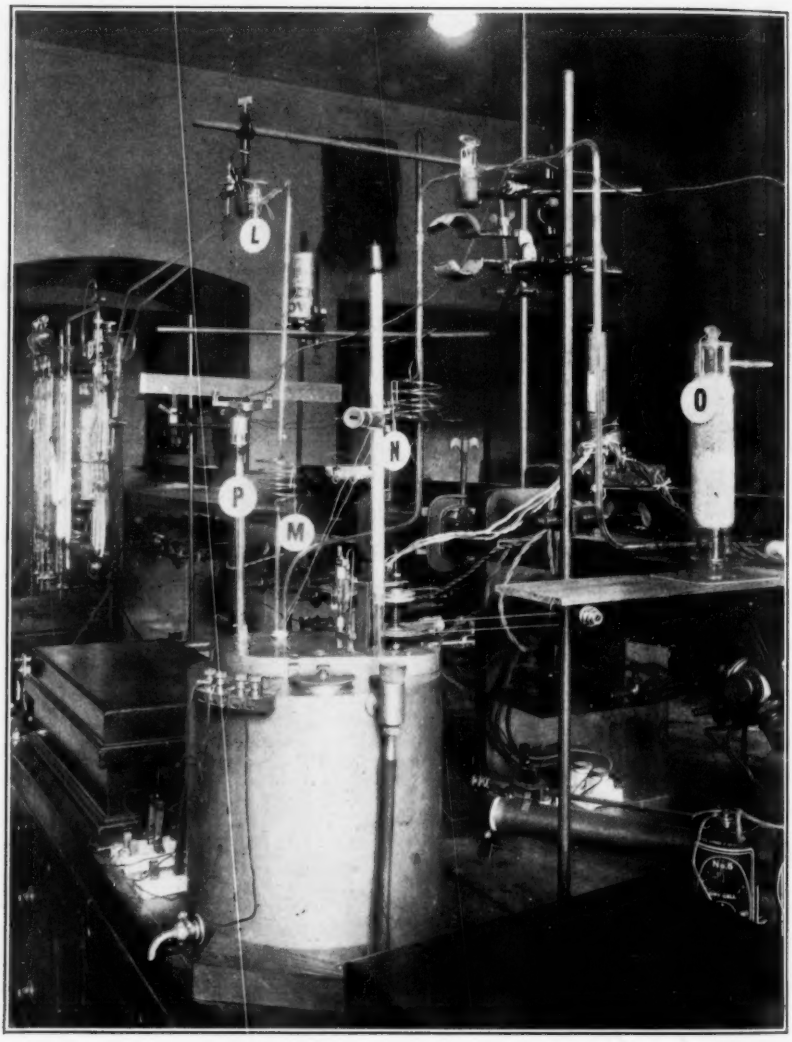

FIGURE 3.—*Calorimeter assembly*

in the absorber less the weight of the air in the balance case displaced by 1 g of brass weights is approximately 0.0008 g per gram of SO_2. This correction must be added to the apparent weight of each gram of SO_2 absorbed in order to obtain the true mass. This only approximated the true state of affairs, however, because a portion of the "ascarite" in the absorber was changed to Na_2SO_3, and because some of the water in the "ascarite" was transferred to subsequent layers of "ascarite" and to the drying agent at the exit end of the tube. All of these possible changes produce a volume change different from that calculated above.

In the first calorimetric experiments three ground glass joints between the calorimeter and the absorber were lubricated with grease, and the SO_2 reacted with it to form a product which was caught in the absorber, resulting in too large a weight for the SO_2. When this trouble was avoided by using deKhotinsky cement on the joints, and when the absorption of moisture from the room air by the drying agent in the exit end of the absorder was prevented by the use of a suitable guard tube, the number of moles of SO_2 absorbed was equal, within the limits of the correction to vacuum and the precision of the weighings of the absorber, to the number of moles of sulphur used up in the reaction as determined by the loss in weight of the sulphur in the reaction chamber. This is shown by the following results:

Run	Mole of S	Mole of SO_2	Ratio $\frac{\text{Mole of } SO_2}{\text{Mole of S}}$
R	0.12215	0.1222_8	1.001_1
S	.14101	$.1409_2$	$.999_4$
T	.13257	$.1327_3$	1.001_1
X	.14069	$.1407_4$	1.000_4

The SO_2 absorber, which had a weight of about 400 g, was weighed to 0.001 g, with a counterpoise of identical dimensions.

In calculating the heat of formation of SO_2, the number of moles of SO_2 formed was in all of the experiments taken as equal to the number of moles of sulphur which disappeared from the reaction chamber.

IV. THE CALORIMETRIC APPARATUS AND ACCESSORY INSTRUMENTS

1. THE CALORIMETER

The calorimeter (Bureau of Standards inventory No. 13211) used in this work is very similar to the one described by Dickinson.[11] The calorimeter assembly is shown in Figure 3, and a schematic cross section is shown in Figure 4. The important parts of the

[11] H. C. Dickinson, B. S. Bulletin, **11**, p. 189; 1915. B. S. Sci. Paper No. 230; 1914.

calorimeter assembly are designated in Figure 4 with letters: *A*, water jacket, which was maintained at a constant temperature with the heater *H* controlled with a toluene-mercury thermostatic regulator and relay in the jacket heater circuit; *B*, jacket stirrer; *C*, calorimeter can filled with water; *D*, platinum resistance thermometer for determining the temperature of the calorimeter water; *E*, calorimeter stirrer; *F*, Beckmann thermometer, by means of which the jacket temperature was read to 0.001° C.; *G*, reaction chamber. An air space of about 1 cm thickness separated the calorimeter can and the jacket.

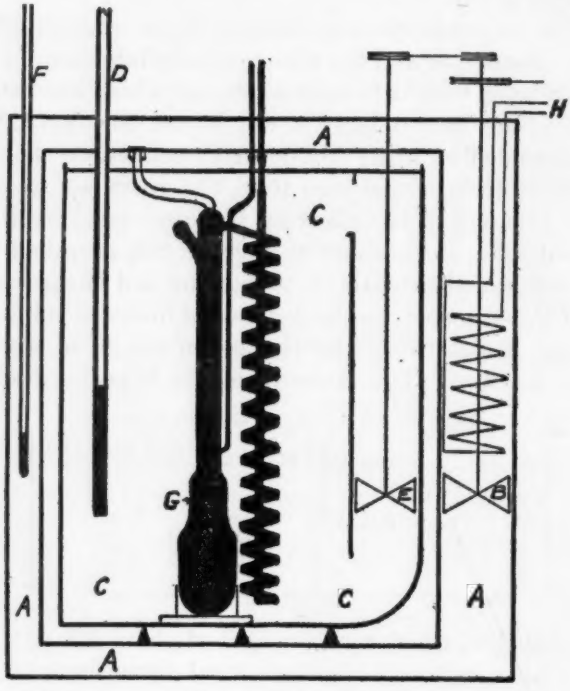

FIGURE 4.—*Schematic diagram of the calorimeter*

In Figure 3, the letter designations are: *L*, two-way stopcock; *M*, gas inlet into calorimeter; *N*, gas exit from the calorimeter; *O*, SO_2 absorber; *P*, platinum resistance thermometer.

The heat transfer from the jacket to the calorimeter increased the temperature of the latter approximately 0.0021° per minute per degree difference in temperature.

The energy given to the calorimeter by its stirrer running at 200 r. p. m. was about 4.0 joules per minute.

The temperature of the jacket did not change more than 0.002° C. in some runs, while in others it changed as much as 0.01° C. Readings of this temperature were taken every 5 or 10 minutes, so that the jacket temperature change was known to 0.001° C. Immediately on

conclusion of a run the platinum thermometer was placed in the jacket, and the Beckmann reading was obtained in terms of the platinum resistance thermometer.

2. THE THERMOMETER

The temperature of the calorimeter was determined with a calorimetric type platinum resistance thermometer (Bureau of Standards mark Pt 10). The resistance of the thermometer was read on a Leeds & Northrup, 8067, Mueller type Wheatstone bridge with a Leeds & Northrup type 2500R galvanometer whose scale was 1 m distant. One millimeter on the galvanometer scale corresponded to 0.0001 ohm (about 0.001° C.). The bridge was balanced to the nearest 0.0001 ohm and the next figure, corresponding to about 0.0001° C., was interpolated from the galvanometer deflections. The bridge was calibrated at the beginning of the investigation.

The platinum resistance thermometer had previously been used in the heat division of the bureau, and its calibration data then were: $R_0 = 25.6227$ ohms; $R_{100} - R_0 = 10.0136$ ohms; $\delta = 1.487$. R_0 was again measured at the beginning of this work and found to be 25.6230 ohms, which value was found unchanged at the end of the investigation.

Eliminating pt from the Callendar formula,

$$t = \mathrm{pt} + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100}$$

$$\mathrm{pt} = \left(\frac{R - R_0}{R_{100} - R_0}\right)100$$

and rearranging, one obtains:

$$R = R_0 + \frac{R_{100} - R_0}{100}\left(1 + \frac{\delta}{100}\right)t - \delta\,\frac{(R_{100} - R_0)}{10^6}t^2 \qquad (1)$$

Substituting the values of R_0, $R_{100} - R_0$, and δ, there results the equation giving the resistance R, in terms of t, the temperature in ° C.:

$$R = 25.6230 + 0.101625t - 0.00001489t^2 \qquad (2)$$

Differentiating, one finds

$$\frac{dR}{dt} = 0.101625 - 0.00002978t \qquad (3)$$

$$\frac{d^2R}{dt^2} = -0.00002978 \qquad (4)$$

For 25.00° C., $\frac{dR}{dt} = 0.100880$ ohm per degree, and the change in $\frac{dR}{dt}$ is -0.000030 ohm per degree per degree. In translating a resistance change of several tenths of an ohm into the corresponding

temperature rise in ° C., the resistance change is divided by the proper value of $\frac{dR}{dt}$ for the given average temperature of the rise.[12]

3. THE ELECTRICAL ENERGY SYSTEM

The supply of electrical energy came from a battery of lead storage cells of 30 volts, maintained in the electrical division of the bureau. The current was determined by measuring the potential drop across a standard 0.1 ohm resistance on a Leeds No. 3316 potentiometer. The voltage drop was taken from points on the current leads exactly midway between the calorimeter and the jacket. The leads were in good thermal contact with, but electrically insulated from, the jacket case. A Leeds & Northrup type 2500 galvanometer with scale 1 m. distant was used in conjunction with the potentiometer, whose smallest decade consisted of nine 0.00001 volt steps.

The potentiometer was calibrated, and the resistance of the standard 0.1 ohm measured by the electrical division of the bureau. An

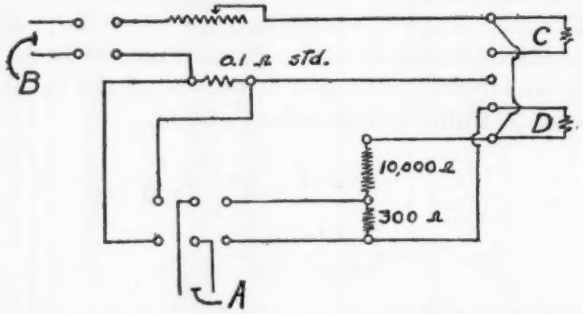

FIGURE 5.—*Diagram of the electrical energy system*

A, to potentiometer; *B*, to storage battery; *C*, substitute resistance; *D*, heating coil in reaction chamber.

Eppley, No. 34701, standard cell, checked against the standards of the bureau, was used with the potentiometer. The stop watch (Bureau of Standards inventory No. 37091E), used to measure the time of the energy input, was calibrated for intervals of 60, 300, and 3,600 seconds by the weights and measures division of the bureau.

A diagram of the electrical circuit is shown in Figure 5. Since a very small part of the current which was measured on the 0.1 ohm standard resistance passed through the 10,300 ohms which are in parallel with the heating coil, a factor of $1-\frac{r}{10{,}300}$ was applied to the measured electrical energy, r being the resistance of the heating coil. The potentiometer measured $\frac{300}{10{,}300}$ of the potential drop across the heating coil. Each of the coils in the two resistance boxes which determined this latter ratio were calibrated in the electrical division of the bureau.

[12] For a complete discussion of this method see H. C. Dickinson and E. F. Mueller, B. S. Bulletin, 9, p. 483; 1913; B. S. Sci. Paper No. 200; 1913.

The actual potentiometer readings for both the current and voltage were about 0.25000 volt and were read and recorded to five significant figures. All the electrical instruments had been calibrated to 0.01 per cent.

It should be pointed out here that the above method of measuring the electrical energy really determines $\frac{E^2}{R}$, and not $E \times I$. With a given current flow, readings of the potential drop across the 0.1 ohm standard resistance and across the heating coil give directly the ratio of the two resistances. For convenience in discussion and calculation, however, the current I will be used in place of $\frac{E}{R}$ throughout this paper.

When electrical energy was supplied to the reaction chamber at a rate of 20 joules per second, the temperature of the heating coil rose to the neighborhood of 400° C., because the vacuum jacket prevented the rapid transfer of energy from the coil to the water in the calorimeter. Because of the rapid increase in the resistance of the platinum coil with the temperature, the current decreased and the voltage drop increased from the initial value until a steady state was reached. The initial value of the current and voltage could be calculated from a knowledge of the initial resistance of the platinum wire, the total resistance in the line, and the voltage of the battery of cells which supplied the energy. The steady state current and voltage were reached in about three minutes, with the greater part of the change occurring in the first minute.

In every run two readings of the voltage and two of the current were made in the first minute, then a reading every half minute. These readings, along with the calculated initial current and voltage, when plotted, gave curves similar to that in Figure 6. The energy during the first period of the rapidly changing resistance was found by calculating, from the curves, the product of the average voltage and average current for each 12-second interval for the first minute, and then for each 30-second interval until the last half minute of the 4-minute period, when two 15-second intervals were taken. In the SO_2 experiments, the oxygen was turned on 3½ minutes after the current was switched on, and the added increase in temperature and resistance of the coil due to the reaction energy was evidenced by a sudden small jump in the voltage and a drop in the current. This is shown in Figure 6. The electrical energy supply for the sulphur runs was cut off at the end of the fourth minute.

The energy curves for the calibration runs were similar to those for the SO_2 experiments except that the current and voltage were practically constant after the third minute until the electrical energy was cut off at the end of the heating time of 50 to 60 minutes.

V. MOLECULAR WEIGHTS, CONSTANTS, FACTORS, UNITS, ETC.

The atomic weight of sulphur was taken as 32.065 and the molecular weight of SO_2 as 64.065.

All weighings, both of sulphur and of water, were corrected to vacuum, with the factors 1.00044 and 1.00106, respectively. In calculating these factors, the following densities, in g/cm³, were used: Brass weights, 8.4; dry nitrogen in the reaction chamber, 0.00117; water, 0.998; air in the balance case, 0.0012; rhombic sulphur, 2.07.

The electrical energy was measured in international joules, since the instruments had been calibrated in terms of the international

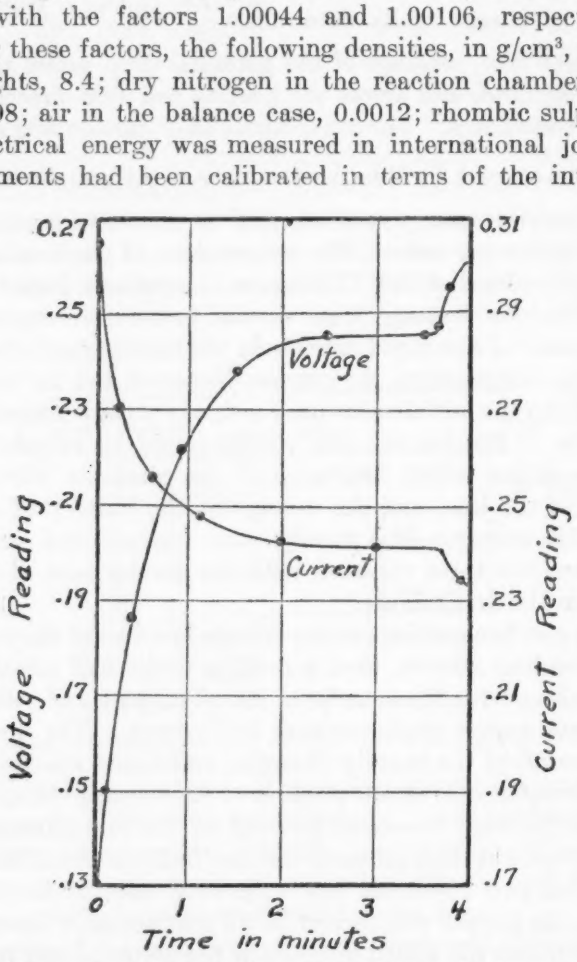

FIGURE 6.—*Time variation of the current and voltage in a sulphur experiment*

ohm and the international volt. In converting the final value for the heat of formation of SO_2 from international to absolute joules, 1 international joule was taken to equal 1.00034[13] absolute joules.

For the purpose of comparing the heat capacities of the slightly different amounts of water which were used in the various experiments, and the slightly different mean temperatures of the experi-

[13] See the report of E. C. Crittenden, J. A. I. E. E., 46, No. 8, p. 769, 1927.

ments, the heat capacity of water at 25° C. was taken as 4.178 joules per gram per degree and its temperature coefficient[14] at 25° C. as −0.0005 joule per gram per degree per degree.

VI. THE CALORIMETRIC PROCEDURE

1. CALIBRATION EXPERIMENTS

The calorimetric procedure consisted in determining the amount of electrical energy which would bring about a temperature rise in the calorimeter equivalent to that produced by the formation of a given amount of SO_2 in the same calorimeter and apparatus at the same average temperature under the same operating conditions.

The constant-temperature-jacket method was followed in conducting the experiments. The initial temperatures of the calorimeter and of the jacket were so adjusted that, at the end of a run, the temperature of the calorimeter would be equal to, or slightly below,

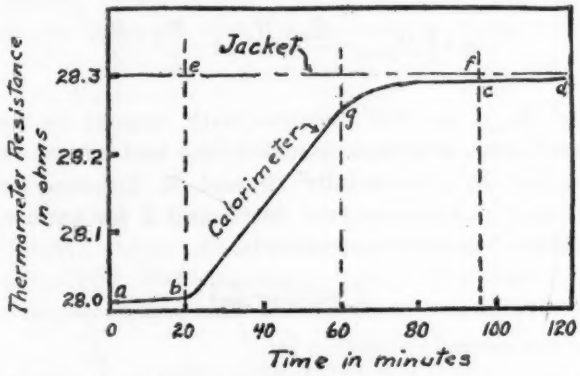

FIGURE 7.—*Time-temperature curve of the calorimeter in a sulphur experiment*

that of the jacket, and the average of the initial and final temperatures of the calorimeter would be 25° C.

A typical time-temperature curve for the calorimeter during a sulphur run is given in Figure 7. The shape of the corresponding curve in the calibration runs was the same except that the time from *g* to *c*, in which temperature uniformity was attained, was 20 instead of 35 minutes as in the sulphur runs. Observations of the calorimeter temperature were made during the period from *a* to *b*. At *b*, energy was supplied to the calorimeter and its temperature rose steadily, and almost linearly, to *g*, when the energy supply, either reaction or electrical, was cut off. Temperature uniformity was attained at *c*, and temperature readings were continued to *d*.

The corrections applied to $R_c - R_b$, which will be designated as ΔR, the main temperature rise, were two: First, a correction which is

[14] Int. Crit. Tables, 5, p. 78.

independent of the temperature difference between the calorimeter and the jacket, and is constant with time; and, secondly, a correction which is directly proportional to the temperature difference between the calorimeter and the jacket. The first correction includes the energy given to the calorimeter through stirring and probably a large part of the energy removed from it through evaporation; and the second correction consists, in a large measure, of the flow of energy from the jacket to the calorimeter. In the following discussion, u is the first correction in "ohms" per minute; k is the proportionality factor, in "ohms" per minute per "ohm," for the second correction; R is the calorimeter temperature and R_j the jacket temperature, both in "ohms," at the time Z, in minutes.

The following equations hold to a high degree of approximation:

$$u+\left(R_{j(a,b)}-\frac{R_a+R_b}{2}\right)k=\frac{R_b-R_a}{Z_b-Z_a} \tag{5}$$

$$u+\left(R_{j(c,d)}-\frac{R_c+R_d}{2}\right)k=\frac{R_d-R_c}{Z_d-Z_c} \tag{6}$$

$R_{j(a,b)}$ and $R_{j(c,d)}$ are the averages with respect to time, of the jacket temperatures over the periods a to b and c to d, respectively. Z_b-Z_a and Z_d-Z_c were usually 20 and 25 minutes, respectively. These two equations were solved for u and k for each experiment. The total value of the first correction is:

$$U=u(Z_c-Z_b) \tag{7}$$

and that of the second correction is:

$$K=k(\text{area } b, g, c, f, e) \tag{8}$$

Z_c-Z_b was usually 75 or 80 minutes.

The corrected temperature rise in "ohms" is then given by the following equation:

$$\Delta R_{\text{corr.}}=(R_c-R_b)-K-U \tag{9}$$

The above method will give the corrected temperature rise to a high degree of precision provided that both k and u are constant over the period of a single experiment; that is, from Z_a to Z_d. The effect of evaporation was minimized by having the calorimeter temperature always below that of the jacket. If the stirring speed is constant, the stirring energy will be constant except for a very small decrease, due to the decrease in viscosity of the water with rise in temperature.

Since, for the procedure adopted in these experiments, the coefficient of k in equation (5) was small compared with that in equation (6), the above method of calculation amounts to determining k at the beginning and u at the end of the experiment. Any small absolute

error in this method of determining the true temperature rise will not affect the final result of the investigation, since the same procedure was followed in both the calibration and sulphur combustion runs.

For a calibration run, the electrical energy input for the first three or four minutes was calculated as explained in Part IV, section 3, and the electrical energy over the remainder of the run was found by taking the product of the average current and voltage. Since dry nitrogen gas at a rate of 70 to 100 ml per minute was passed through the chamber in order to increase the rate of transfer of energy from the heating coil in the reaction chamber to the water surrounding it, proper corrections when necessary were applied to $R_b - R_a$, $R_d - R_c$, and $R_c - R_b$, for the amount of energy given to or removed from the calorimeter by the nitrogen gas. All the appropriate corrections and calibration data were applied to the readings of the potentiometer, the Mueller bridge, the stop watch, the room thermometer, etc.

The following equation was used to calculate the heat capacity of the calorimeter (can, reaction chamber, thermometer) plus the water:

$$C_{p(\text{calor.}+H_2O)} = \frac{\text{elec. energy} + \text{“}N_2\text{ energy”}}{\Delta t_{\text{corr.}}} \qquad (10)$$

The results of seven calibration experiments are given in Table 1. Experiments 1 to 7, inclusive, could not be calculated because of failure to secure a sufficient number of readings in the period of rapidly changing current and voltage or because of difficulties with the jacket heater and thermostatic control. The result of run 10 is obviously not in accord with the others and is omitted in taking the average.

TABLE 1.—*Calibration experiments*

Run	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$	$\Delta t_{corr.}$
	Ohms	*Ohms/min./ohm*	*Ohms/min.*	*Ohms*	*Ohms*	*Ohms*	*Ohms per ° C.*	*° C.*
8	0.63733	0.001994	0.0000566	0.05549	0.00509	0.57675	0.100886	5.7168
9	.39264	.002002	.0000277	.02172	.00221	.35871	.100873	3.6552
10	.40329	.002034	.0000346	.03040	.00277	.37012	.100882	3.6688
11	.40000	.001996	.0000357	.02719	.00286	.36995	.100870	3.6676
12	.30614	.001986	.0000648	.01722	.00421	.28471	.100881	2.8222
13	.40627	.001995	.0000223	.02996	.00178	.37453	.100883	3.7125
14	.40486	.002017	.0000205	.02979	.00164	.37343	.100877	3.7018

Run	Average temp.	Electrical energy	“N_2 energy”	Mass of H_2O	$C_{p(calor.+H_2O)}$	Deviation from the mean
	° C.	*Int. joules*	*Joules*	*g*	*Int. joules* [1]	*Joules*
8	24.80	87,659	+11	3,592.2	15,368	+1.8
9	25.27	55,112	−17	3,531.6	15,360	−6.2
10	24.94	55,824	−8	3,556.6	(15,395)	
11	25.37	55,596	−7	3,551.8	15,359	−7.2
12	25.02	43,203	−2	3,584.4	15,373	+6.8
13	24.91	56,966	−1	3,594.6	15,366	−0.2
14	25.14	56,698	−9	3,586.3	15,371	+4.8
				Mean	15,366.2	±4.5

[1] Corrected to 3,600 g H_2O and 25° C.

The arithmetical mean of the six experiments for the heat capacity of the calorimeter plus 3,600 g H_2O at 25° C. is 15,366.2 joules per degree, with an average deviation from the mean of 0.029 per cent, a "probable error" of the mean of 0.010 per cent, and a maximum deviation from the mean of 0.047 per cent. A calculation of the heat capacity of the calorimeter from the masses and heat capacities of its parts, including the partly immersed platinum thermometer, assuming the heat capacity of water to be 4.178 joules per gram per degree at 25° C., gave a result of 15,373 joules.

2. SULPHUR DIOXIDE EXPERIMENTS

The SO_2 experiments were made under exactly the same conditions as the calibration experiments, and the time-temperature curves were similar except that a longer time was required to reach temperature uniformity at the end of the run because of the presence of sulphur in the chamber.

Two special runs, α and β, were made to determine approximately how much of the remaining sulphur failed to return to the rhombic form in the time Z_g to Z_c. In these two runs no sulphur was burned, but electrical energy supplied to the calorimeter at the usual rate for 4 minutes in run α and 10 minutes in run β. Since the heat content of monoclinic sulphur is greater than that of rhombic sulphur, the following equation should hold:

$$\text{electrical energy} = \Delta t_{corr.}\, C_{p(calor.+H_2O+S)} + q \qquad (11)$$

where q is the energy which has been retained by that portion of sulphur which has not returned to the rhombic form. The results of the two runs are:

Run	g sulphur in chamber	q
		Joules
α	8	15
β	10	14

This is about 1.5 joules per gram of suphur remaining in the chamber. Since the heat absorbed when 1 g of rhombic sulphur changes to the monoclinic form is about 9 joules, this calculation indicates that only a small part (one-sixth, if the data be treated as exact) of the sulphur remained in the monoclinic form in these experiments. Presumably this remaining small amount of monoclinic sulphur was changing very slowly, so that its effect on the value of $R_a - R_c$ is negligible.

A sample data sheet giving the readings for an SO_2 experiment is given in Table 2. Appropriate corrections were applied to the readings as in the case of the calibration experiments. The heat capacity of the calorimeter plus 3,600 g H_2O was taken as 15,367

joules per degree (15,366.2 + 0.8, because a small amount of ground pyrex glass, having a heat capacity of 0.8 joule per degree was later placed in the cooling coil of the reaction chamber) plus the heat capacity of the sulphur remaining in the chamber plus the heat capacity of one-half of the sulphur used up in the experiment. This last addition to the heat capacity of the system was necessary because the temperature of the experiment was taken as the average of the initial and final temperatures.

The heat of formation of 1 mole of SO_2 at the average temperature of the experiment was calculated by the following formula:

$$Q_t = \frac{\Delta t_{corr.} C_{p(calor.+H_2O+S)} - [\text{elec. energy} + \text{"}O_2, N_2\text{, energy"} + \text{"Tr. energy"}]}{m} \quad (12)$$

in which m is the number of moles of sulphur converted to SO_2; "O_2, N_2, energy" is the energy given to the calorimeter by the oxygen and nitrogen gases; "Tr. energy" is the energy involved in the transformation of rhombic to monoclinic sulphur, and was taken as -1.5 joules per gram of sulphur remaining in the chamber. The "O_2, N_2 energy" correction was calculated by determining the average (with respect to time) temperature of the incoming gases and of the calorimeter water. The difference of these two temperatures multiplied by the heat capacity of all the incoming gases gives the value of the correction. If the mean-time temperature of the calorimeter was below that of the incoming gases, energy was given to the calorimeter by the gases. At any given time the SO_2 gas left the calorimeter at the temperature of the calorimeter water.

TABLE 2.—*Sulphur dioxide experiment No. X*

Time		Amperes	Volts	Time	Pt thermometer (calorimeter)	Beckmann thermometer (jacket)	Room temperature	O_2 gage	N_2 gage
Min.	*sec.*			*Min.*	*Ohms*	*Degrees*	*°C.*	*mm*	*mm*
20	00	(0.305)	(0.130)	0 (a)	25+3.02620	1.704	24.6		
	05		.150	1	3.02694				
	12	.270		5	3.02988				
	23		.190	10	3.03350	1.704	24.8		
	28	.260		15	3.03710				
	40		.210	19	3.03998				
21	08	.248		20 (b)	(3.04070)	1.704	24.9		
				23½				(on) 10.5	
	30		.2382	25	3.0628			10.0	
22	00	.2422		26	3.0694				
	30		.2460	30	3.0972	1.706	25.0	10.0	
23	00	.2413		35½	3.1395	1.706			
	30		.2466	40	3.1752	1.706	25.0	10.0	
	38		.2466	45	3.2148	1.706			
	45		.256	50	3.2540	1.706	25.2	10.0	
	55		.261	55	3.2926	1.706			
				60 (g)	3.3305	1.706	25.2	10.0	
				61¼				(off) 10.0	(on) 7.0
				65	3.3544	1.708			9.0
				70	3.3595	1.706	25.3		13.0

Energy time (stop watch) 4 min., 0.8 sec.

TABLE 2.—*Sulphur dioxide experiment No. X*—Continued

	Time	Pt thermometer (calorimeter)	Beckmann thermometer (jacket)	Room temperature	O_2 gage	N_2 gage
	Min.	*Ohms*	*Degrees*	°C.	*mm*	*mm*
Volt ratio: $\frac{10300}{300}$	75	3.36145	1.706			
	80	3.36227	1.706	25.3		13.0
Mass sulphur: 4.5112 g	85	3.36266	1.707			
	90	3.36287	1.707	25.2		(off) 13.0
Mass water: 3,603.0 g	95 (c)	3.36304	1.708			
	100	3.36318	1.708	25.2		
Mass SO_2:9.016$_5$ g	105	3.36332	1.709			
	110	3.36347	1.710	25.2		
	115	3.36360	1.708			
	120 (d)	3.36374	1.708	25.1		
	125	3.3694 ~	1.708	Correction: −0.4° C.	10.0 mm ~ 0.10 *L* per min.	13.0 mm ~ 0.13 *L* per min.

For the reaction

$$S_{rh.\ (solid)} + O_{2\ (gas)} = SO_{2\ (gas)} \cdot (25°\ C.) \qquad (13)$$

the increase in heat capacity, Δc_p, is −12 joules per degree per mole. This very small correction was applied in calculating the values of Q_{25} from those experiments which were made at average temperatures slightly different from 25° C. In obtaining this value of Δc_p, the following heat capacities, in joules per mole per degree, were used: S, 23; O_2, 29.4; and SO_2, 40.6.

TABLE 3.—*Sulphur dioxide experiments (first series)*

Run	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$	$\Delta t_{corr.}$
	Ohms	*Ohms/min./ohm*	*Ohms/min.*	*Ohms*	*Ohms*	*Ohms*	*Ohms/°C.*	°C.
A	0.38213	0.001960	0.0000670	0.02288	0.00603	0.35322	0.100878	3.5016
B	.39599	.001971	.0000071	.02405	.00064	.37130	.100892	3.6802
C	.38263	.001980	.0000069	.02194	.00062	.36007	.100892	3.5689
D	.24225	.001936	.0000142	.01051	.00107	.23067	.100880	2.2866
E	.30065	.001939	−.0000025	.01165	−.00018	.28918	.100881	2.8665
G	.27847	.002022	.0000035	.01226	.00018	.26603	.100880	2.6371
H	.27863	.001981	.0000086	.01270	.00060	.26533	.100864	2.6305

Run	Average temperature	Mass of H_2O	C_p (calor.+H_2O+S)	Electrical energy	"O_2, N_2 energy"	"Tr. energy"	Moles of S	Correction to 25.00° C [1]	$Q_{t,25°C}$	Deviation from the mean.
	°C.	*g*	*Int. joules/°*	*Int. joules*	*Joules*	*Joules*		*Joules/mole*	*Int. joules/mole*	*Joules*
A	25.24	3,602.6	15,383	5,341	−24	−6	0.16370	−3	+296,600	−130
B	24.58	3,588.1	15,324	4,687	−22	−5	.17441	5	296,630	−100
C	24.59	3,581.8	15,298	4,690	−14	−6	.16826	5	296,730	0
D	24.99	3,593.7	15,347	4,739	−19	−10	(.10265)	0	(296,000)	
E	24.97	3,603.5	15,388	4,546	−30	−8	.13331	0	297,050	+320
G	25.01	3,613.8	15,431	4,990	−19	−10	.12033	0	296,950	+220
H	25.52	3,604.9	15,393	5,100	−21	−10	.11950	−6	296,420	−310
								Mean..	+296,730	±180

[1] This correction = $(\Delta C_p) \times$ (average temperature − 25.00°C.). $\Delta C_p = -12$ joules per mole per degree.

TABLE 4.—*Sulphur dioxide experiments (second series)*

Run	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$	$\Delta t_{corr.}$
	Ohms	*Ohms/min. ohm*	*Ohms/min.*	*Ohms*	*ohms*	*Ohms*	*Ohms/°C.*	*°C.*
R	0.28106	0.002053	0.0000128	0.01227	0.00096	0.26783	0.100865	2.6553
S	.32202	.002023	−.0000019	.01617	−.00014	.30599	.100871	3.0334
T	.30350	.001978	.0000139	.01392	.00104	.28854	.100870	2.8605
U	.31046	.001987	.0000242	.01465	.00181	.29400	.100868	2.9146
V	.33854	.002108	.0000038	.01802	.00029	.32023	.100865	3.1748
W	.32501	.002091	.0000182	.01796	.00136	.30569	.100865	3.0307
X	.32260	.002119	.0000151	.01707	.00113	.30440	.100866	3.0179

Run	Average temperature	Mass of H_2O	C_p (calor.+ H_2O+s)	Electrical energy	"O_2,N_2 energy"	"Tr. energy"	Moles of S	Correction[1] to 25.00° C.	$Q_{,25°C.}$	Deviation from the mean
	°C.	*g*	*Int. joules /°*	*Int. joules*	*Joules*	*Joules*		*Joules/ mole*	*Int. joules/ mole*	*Joules*
R	25.50	3,606.8	15,399	4,689	−17	−6	0.12215	−6	+296,540	−280
S	25.29	3,595.8	15,355	4,737	−22	−8	.14101	−3	296,920	+100
T	25.35	3,605.1	15,393	4,703	−22	−8	.13257	−5	296,900	+80
U	25.41	3,609.0	15,412	4,586	−6	−12	.13591	−5	296,960	+140
V	25.49	3,595.8	15,357	4,597	−14	−12	(.14930)	−6	(295,930)	----------
W	25.50	3,587.8	15,322	4,551	−11	−11	.14115	−6	296,850	+30
X	25.48	3,603.0	15,386	4,705	−13	−13	.14069	−6	296,730	−90
								Mean..	+296,820	±120

[1] See footnote to Table 3, p. 614.

The results of the SO_2 experiments are given in Tables 3 and 4. Run F was lost. After run H was completed, some trouble developed in the oxygen line, but it was not until run Q was completed that the trouble was definitely located. The oxygen line was completely renovated, and then runs R to W were made. A time of one month elapsed between the two series of experiments. In calculating the average of the experiments, runs D and V were omitted as they are not in agreement with the others.

VII. RESULTS

The results of the two series of SO_2 experiments are:

	Series I	Series II
Arithmetical average[1] of the series ..... joules	296,730	296,820
Average deviation from the mean ..... per cent	.061	.040
Maximum deviation from the mean ..... do	.108	.094
"Probable error" of the mean ..... do	.022	.015

[1] The geometrical mean of the results is the same within 10 joules for the two series, while an average obtained by weighting the results according to the number of moles of SO_2 formed leaves the average of the second series unchanged in the fifth figure and lowers that of the first series by 10 joules.

Because of the more proficient technic in the second series, as evidenced by the smaller deviations, the averages of the two series have been weighted inversely as the squares of their average deviations and the final "best value" taken as +296,790 international joules, with an average deviation from the mean of 0.047 per cent.

The results of the calibration experiments (Table 1) showed an average deviation of 0.029 per cent. Since the value used for the heat capacity of the calorimeter plus 3,600 g H_2O, enters into the calculation of Q, the heat of formation of SO_2, the "best value" for Q may be assigned a precision measure of

$$\sqrt{(0.029 \text{ per cent})^2 + (0.047 \text{ per cent})^2} = 0.055 \text{ per cent},$$

or 165 joules.

A conservative value for the possible error in the final result due to all known causes may be placed at ± 200 joules, or 0.067 per cent.

The heat of formation of 1 mole of SO_2, from gaseous oxygen and rhombic sulphur at 25° C., is, then, $+296{,}790 \pm 200$ international

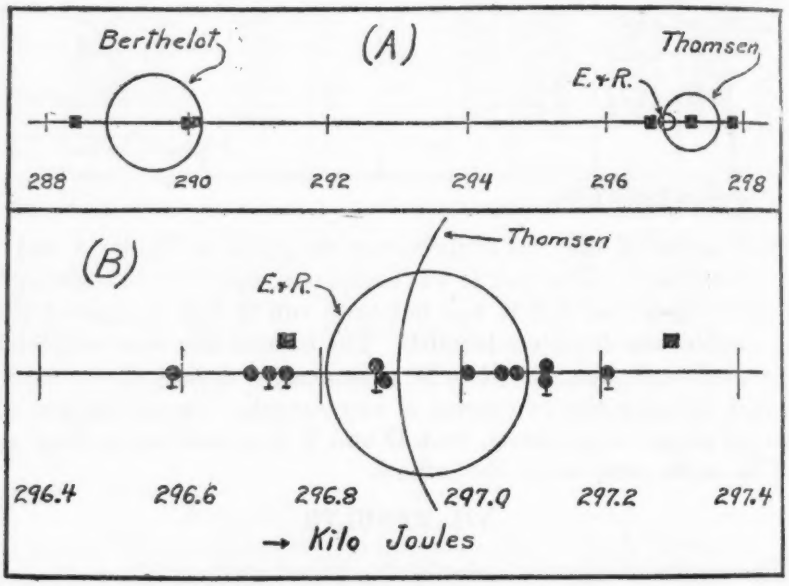

FIGURE 8.—*A graphical comparison of the data*

joules; or, using the factor 1.00034, $+296{,}890 \pm 200$ absolute joules. This latter value, divided by 4.185, gives $+70{,}940 \pm 50$ g-cal.$_{15}$.

In Figure 8 (*A*), a comparison of these results with those of Thomsen and of Berthelot is shown graphically. The circles are drawn in each case with a radius equal to the average deviation as reported by the investigators. The average values of Thomsen and Berthelot are, respectively, $+297{,}300$ and $+289{,}600$ joules per mole.[15] The solid squares represent the three measurements of Thomsen and the three

[15] In converting the results of Thomsen and of Berthelot from calories (about 18°C.) to absolute joules, the factor 4.182 was used. Then, since their reactions were carried out at 16° to 20°C., the ΔC_p correction (Pt. VI, sec. 2) was applied.

of Berthelot. The Thomsen circle almost completely incloses the E. and R. circle, showing that within the limits of his average deviation, the results obtained by Thomsen are in accord with those of the present investigation. Figure 8 (*B*) shows an enlarged view of that portion of Figure 8 (*A*) which contains the results of Thomsen and of E. and R. The small solid circles are the result of this work—the appendage identifying the results of Series I. The two solid squares are the two lowest of Thomsen's values.

Figure 9 shows a plot of the deviations of the various experiments as a function of the number of moles of sulphur converted to SO_2 in

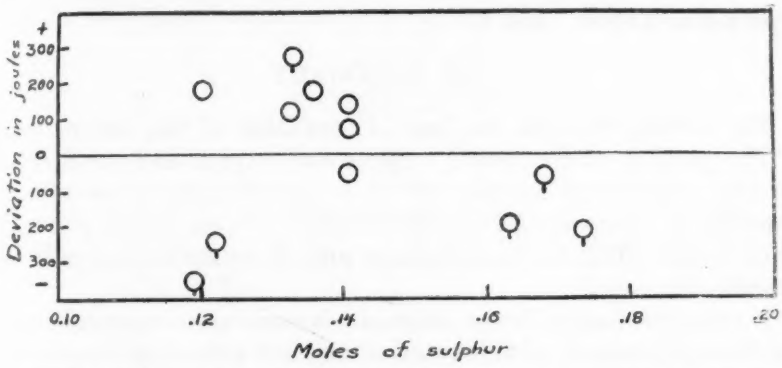

FIGURE 9.—*A plot of the deviations as a function of the number of moles of sulphur in a given experiment*

the given experiments. No trend of the deviation with the amount of sulphur is evidenced by this plot. The circles with appendages refer to the experiments of the first series.

TABLE 5.—*Analysis of the measured quantities in the calibration experiments*

$$C_{p(\text{calor.}+H_2O)}=\frac{EIZ\ (0\text{ to }4\text{th min.})+EIZ\ (\text{from 4th min. on})+\text{"}N_2\text{ energy"}}{\Delta t-U-K}$$

Quantity	Magnitude	Estimated average error	Percentage effect on $C_{p\cdot(\text{calor.}+H_2O)}$
			%
Electrical energy *EIZ* (0 to 4th min.)	4,800 j	± 3 j	±0.006
Electrical energy:			
E voltage	5.9 volts	±0.0006 volts	.010
I current	2.5 amps	± .00025 amp	.010
Z time	2,700 sec	± .2 sec	.007
$E\times I\times Z$ (4th min. on)	40,000 j	±6 j	.015
"N_2 energy"	10 j	±2 j	.005
Δt	3.2°C	± .0005°C	.017
U	.02°C	± .0005°C	.017
K	.2°C	± .001°C	.033
$\Delta t_{corr.}=\Delta t-U-K$	3.0°C	± .0012 °C	.040
$C_{p\ (\text{Calor.}+H_2O)}$	15,300 j	±6.5 j	.043

Table 5 gives an analysis of the estimated average errors in the measured quantities of the calibration experiments. The resultant percentage error is the square root of the sum of the squares of the individual percentage errors. The error in measuring the mass of water in the calorimeter was negligible. The final estimated average error is slightly larger than the average deviation of the actual experiments as reported in Table 1. A like analysis for the sulphur experiments would be similar except that the second or main *EIZ* term is omitted and the measurement of the mass of sulphur used up is included. The final estimated error of the sulphur runs was about equal to the average deviations of the experiments themselves as reported in Tables 3 and 4.

VIII. SUMMARY

The existing data on the heat of formation of SO_2 are reviewed. The problem of combining sulphur and oxygen to form SO_2 with no SO_3 was solved by the use of a special calorimetric reaction chamber in which oxygen was introduced into an excess of hot sulphur vapor. This reaction chamber and its method of operation are described in detail.

A complete description of the methods used in the chemical and the calorimetric control of this reaction and the procedure employed in recording and calculating the data are given.

The value obtained in this investigation for the heat of formation of one mole of gaseous SO_2 from solid rhombic sulphur and gaseous oxygen at 25°C. is $+296{,}890 \pm 200$ absolute joules, or $+70{,}940 \pm 50$ g-cal.$_{15}$. This is compared with the results obtained by Berthelot and by Thomsen.

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